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NAVAL RESEARCH
WASHINGTON, D. C.

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RESEARCH IN NITROPOLYMERS AND THEIR APPLICATION TO SOLID SMOKELESS PROPELLANTS

Contract N7 onr-462
Task Order I

3 April 1953

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Task Order I

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No. of Pages: 112

Period Covered:

16 November 1952 through 15 February 1953

AEROJET-GENERAL CORPORATION

Azusa, California

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CONTENTS

CONTENTS (cont.)

CONTENTS (cont.)

CONTENTS (cont.)

CONTENTS (cont.)

Table

CONTENTS (cont.)

CONTENTS (cont.)

CONTENTS (cont.)

CONTRACT FULFILLMENT STATEMENT

This quarterly report is submitted in partial fulfillment of Contract N7onr-462, Task Order I.

I. SUMMARY

A. This quarterly summary covers research conducted in partial fulfillment of Contract N7onr-462, Task Order I, during the period from 16 November 1952 through 15 February 1953.*

B. The more important results are summarized below:

1. Chain-transfer studies of nitro compounds have been concluded with the final determination of the chain-transfer effects of bromotrinitromethane. The results obtained to date are adequate to explain the irregularities in the polymerization of nitromonomers. A special report on this subject will be issued in the near future.

2. A thorough study of the polymerization of 2,2-dinitrobutyl acrylate has been started. This study is important for the development of formulations with both nitropolymers and inorganic oxidizers.

3. The study of the catalytic effect of chelated-metal compounds on polyurethane formation has been continued. Rate studies have revealed that ferric acetylacetonate is the most effective catalyst for nitropolyurethane formation. It acts about 27 times faster than vanadyl acetylacetonate.

4. Stability studies on postnitrated polyurethanes have been continued. It has been found that a sustained washing of polyurethane I-JN with warm sodium bicarbonate solution at elevated temperature gives a stable product without degradation of the polymer chain.

5. Previous work revealed the dependence of the molecular weight of nitropolyurethanes on the monomer concentration. It has been observed that higher monomer concentrations cause formation of insoluble polymers if the temperature during the polymerization is allowed to rise too rapidly or "run away." Further experiments proved that a linear relationship exists between monomer concentration and relative viscosity.

6. The progress in polyurethane formation is measured by determination of the solution viscosity. It has been shown experimentally that there is a close correspondence between solution viscosity and relative viscosity.

7. The osmometric determination of the molecular weight of nitropolymers is being studied with regard to possible errors in the method; in particular, the effect of diffusion of small polymers requires evaluation.

8. Calculations of the specific impulses of mixtures of various nitropolymers with ammonium nitrate and ammonium perchlorate show that low-energy nitropolymers can be greatly improved by the incorporation of a small amount of oxidizer.

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*Previous work on this contract was covered in Aerojet Reports No. 330, 345, 371, 386, 386A, 404, 416, 417, 417A, 424, 457, 461, 468, 482, 494, 495, 515, 540, 563, 590, 622, 638, and 663.

9. Formulation studies involving the polymerization of nitroacrylates in the presence of dispersed nitropolyurethanes have been conducted. 2,2-Dinitrobutyl acrylate polymerizes in the presence of polyurethane I-J, with which it is incompatible. However, neither 2,2-dinitrobutyl acrylate nor methyl methacrylate gave a cured product with satisfactory properties.

10. A formulation of polyurethane I-A with ammonium nitrate has been prepared by molding a 1:1 mixture at 150°F and 7000 lb/sq inch. The burning rate of this composite at 1000 lb pressure at 60°F was 0.12 in./sec, or approximately the rate determined for the starting polyurethane I-A alone.

11. Warburg-manometer measurements and the potassium iodide starch-paper test are both valuable methods for the determination of the stability and the acceptability of nitropolymers. However, no correlation between these two tests has yet been found.

12. A new polymerizable acrylate, 3,3-dinitrobutyl acrylate, has been prepared. The new compound is an isomer of the previously reported 2,2-dinitrobutyl acrylate.

13. 3,3-Dinitrobutyric acid, an intermediate for the preparation of N-2,2-dinitropropyl acrylamide, has been prepared by two procedures: (a) oxidation of 3,3-dinitrobutanol, and (b) oxidation of 5,5-dinitro-2-pentene.

14. A new isocyanate, 6-carbomethoxy-4,4-dinitrohexyl isocyanate, has been prepared. This compound was converted into the ester of 4,4,12,12-tetranitro-7,9-diaza-8-keto-pentadecanedioic acid.

15. The method of preparing cyclic ketal derivatives of nitrodiols, by means of boron trifluoride catalysis, has been applied to a number of diols and extended to carbonyl compounds other than acetone and formaldehyde.

16. Halo nitro compounds react rapidly with zinc metal to form a white precipitate. This precipitate has been found to hydrolyze upon treatment with mineral acid to yield keto compounds.

17. An intensive investigation has been conducted to find a means for converting readily the available nitrosamines into the corresponding nitramines. However, no practical procedure has yet been found.

18. An SPIA data sheet has been prepared for polyurethane I-J, from 3,3-dinitro-1,5-pentane diisocyanate and 2-nitro-2-methyl-1,3-propanediol.

19. A new contract was recently initiated to conduct rheological and ballistic studies on nitropolymers. Up to the present time the major effort on this contract has been concerned with the setup and calibration of new, highly refined equipment for rheological evaluation. Accordingly, no

report will be made on the work at this time. A complete report on work conducted under Contract NOas 53-618-cwill be presented in the next quarterly summary.

II. TECHNICAL PROGRESS: NITROPOLYMERS

A. VINYL POLYMERIZATION

1. Chain-Transfer of Nitro Compounds

a. Introduction

(1) It was previously observed that tetranitromethane acted as an inhibitor in the polymerization of methyl methacrylate while nitroform behaved as a retarder, allowing polymerization to proceed at a reduced rate with no induction period being observed. The question arose as to the difference between the reactions of the two nitro compounds. With tetranitromethane the most likely possibility seemed loss of a nitro group with a trinitromethyl radical stabilized by resonance, e.g.,

$$C(NO_2)_4 + R\cdot \longrightarrow RNO_2 + O_2N\text{-}\overset{\displaystyle NO_2}{\underset{\displaystyle NO_2}{\overset{|}{\underset{|}{C}}}}\cdot$$

With nitroform it seemed likely that again the radical which would be produced would be the one most stabilized by resonance, e.g.,

$$CH(NO_2)_3 + R\cdot \longrightarrow RH + O_2N\text{-}\overset{\displaystyle NO_2}{\underset{\displaystyle NO_2}{\overset{|}{\underset{|}{C}}}}\cdot$$

Inasmuch as the same radical would be produced in both cases it was difficult to explain the observed differences during polymerization.

(2) In an effort to obtain more information regarding the transfer reaction, bromotrinitromethane was used as a solvent in the polymerization of methyl methacrylate. With this nitro compound one would expect scission of the weakest bond, i.e., the carbon-bromine bond.

b. Discussion

(1) When bromotrinitromethane was added to methyl methacrylate it was found to transfer quite readily. However, it did not inhibit polymerization. It behaved in a manner very similar to nitroform, except that it transferred more readily. Another similarity to nitroform was found upon plotting the solvent-to-monomer ratio against the reciprocal of the

degree of polymerization. As with nitroform, a curve which implied a lower chain-transfer constant at a higher concentration was obtained. As yet the phenomenon is unexplained. The data are presented in Table I.

TABLE I

POLYMERIZATION OF METHYL METHACRYLATE IN THE PRESENCE OF BROMOTRINITROMETHANE

Solvent/Monomer	% Conversion	$[\eta]$	$\bar{P}_n$	$1/\bar{P}_n$	C_T
0	2.92	3.15	7500	1.33×10^{-4}	—
1.11×10^{-3}	3.05	0.464	680	1.47×10^{-3}	1.2
2.48×10^{-3}	3.08	0.274	350	2.86×10^{-3}	1.1
4.96×10^{-3}	3.33	0.205	244	4.10×10^{-3}	0.80
				Average	1.0

(2) The conversion vs time curves and $1/\bar{P}_n$ vs S/M curve are shown in Figures 1 and 2.

2. 2,2-Dinitrobutyl Acrylate

a. Introduction

(1) Based on the results of the chain-transfer study of nitro compounds, the trinitromethyl group is unsuitable as a high-energy grouping in a vinyl monomer. The high chain-transfer of this group leads to polymers with low molecular weights, which are brittle when molded and tend to be thermally unstable. Such materials, even though they possess high specific impulses, are unsuitable as propellants when used alone. The specifications which would be set up for a useful propellant could not be met by these low-molecular-weight polymers.

(2) It should be pointed out that behavior of the trinitromethyl group in a monomer is a blow to the synthetic work of the program. Thus, esters of trinitroethanol are ruled out, and the chemistry of nitroform and its reaction products is no longer of value in making high-energy vinyl monomers. New reactions must be developed and new nitro groupings must be synthesized in order to offset the loss of the nitroform reactions.

(3) One obvious means of obtaining polymers of higher molecular weight is to use a monomer containing nitro groups which chain-transfer less readily. At the present time the only monomer available in sufficient quantity for the study of its polymerization characteristics is

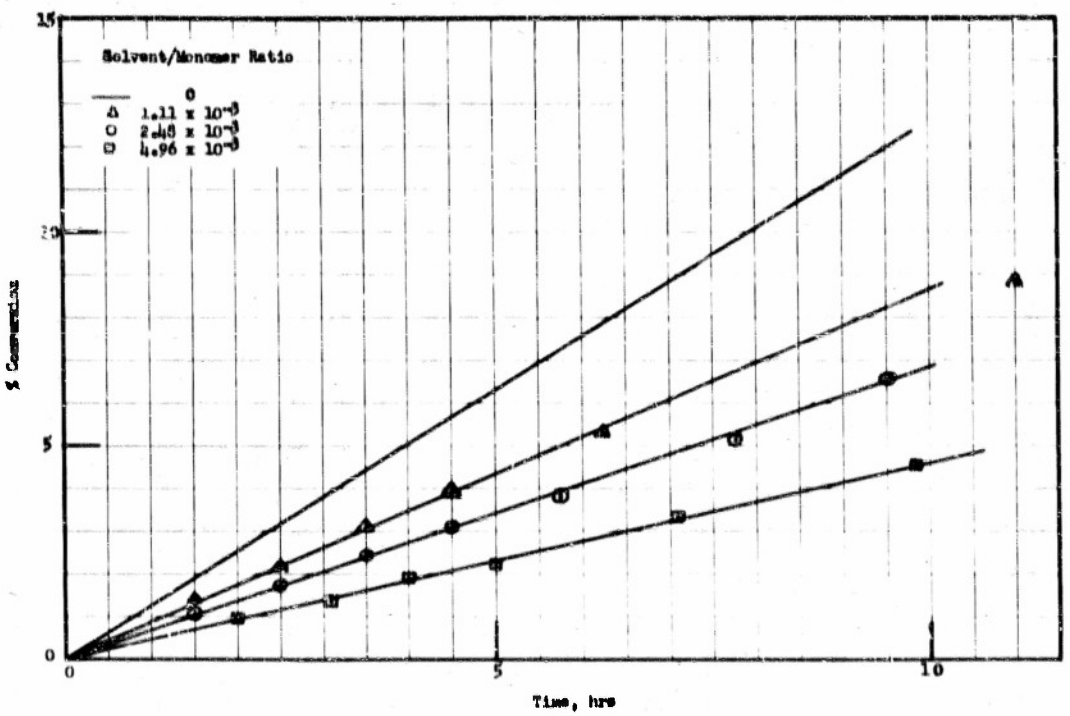

Figure 1

Rate of Polymerization of Methyl Methacrylate in the Presence of Bromonitroform

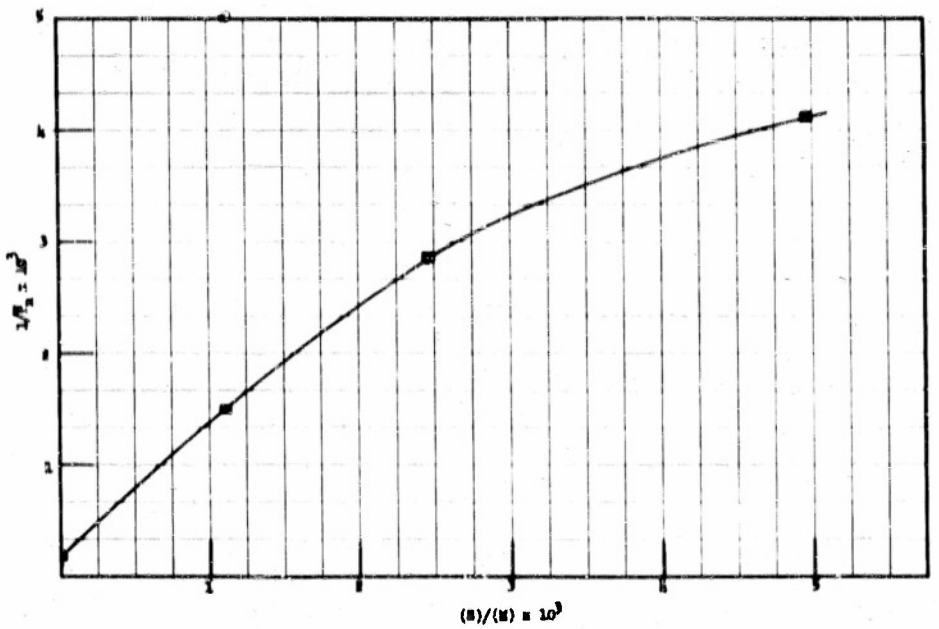

Figure 2

Plot of $1/\overline{P}_n$ vs (S)/(M) for Methyl Methacrylate with Bromonitroform

dinitrobutyl acrylate. It is known to polymerize readily, giving a polymer with a molecular weight of approximately 100,000. Although poly-2,2-dinitrobutyl acrylate is too low in specific impulse to be used as a monopropellant it may be of value as a fuel component in composite propellants or as a coating material in the desensitization of RDX. Currently, it is being used in formulation work as a fuel, with high-energy condensation polymers as the oxidizer component.

(4) Inasmuch as 2,2-dinitrobutyl acrylate promises to be a useful monomer it is desirable to obtain quantitative information regarding its polymerization. Hence a study was initiated to determine the variation of rate and molecular weight with catalyst concentration and to obtain the overall activation energy of polymerization. It was previously reported that 2,2-dinitrobutyl acrylate produced an insoluble polymer upon polymerization.* It was also observed that certain impurities inhibited polymerization. An intensive investigation was carried out to characterize pure 2,2-dinitrobutyl acrylate and to develop a suitable process for producing it.** Thus, only recently has pure 2,2-dinitrobutyl acrylate been available in sufficient quantity for study.

b. Discussion

The polymerization of 2,2-dinitrobutyl acrylate is being studied using azo-bis-isobutyronitrile as catalyst. Thus far, bulk polymerizations have been carried out with the results shown in Table II. The results are not consistent, but it is expected that further work will clarify the discrepancy.

TABLE II

VARIATION OF RATE OF POLYMERIZATION OF 2,2-DINITROBUTYL ACRYLATE WITH CONCENTRATION OF AZO-bis-ISOBUTYRONITRILE

Catalyst Concentration (mole/liter)	Rate (mole/liter/sec)
0.00974	3.9×10^{-5}
0.0182	6.1×10^{-5}
0.0272	6.5×10^{-5}

c. Experimental

(1) The catalyst is weighed into a volumetric flask, and monomer is added at 20°C to the mark on the flask. After mixing, 5-ml

*Aerojet Report No. 590.

**Aerojet Report No. 622.

aliquots are placed in 18 x 150-mm Pyrex test tubes which have been cleaned in cleaning solution and thoroughly washed. The tubes are purged with nitrogen and stoppered with rubber stoppers encased in polythene film. The samples are placed in a 45°C water bath and removed after various time intervals. Upon removal, the sample is cooled in dry ice and the polymer is precipitated by pouring the sample into ca. 100 ml of methanol.

(2) It has been observed that the polymer retains some monomer which is difficult to remove; the following procedure has been found to give satisfactory results: The polymer obtained from the initial precipitation is dissolved in acetone (5 ml for every 1 g of polymer), and the polymer is precipitated by pouring the solution into methanol cooled with dry ice. The polymer is then transferred to fresh methanol at room temperature. The dissolved carbon dioxide expands the polymer to a very porous material. It is removed from the methanol and dried over P_2O_5 by pumping off excess solvent at 1 mm for several hours. The material is obtained as a porous, somewhat brittle mass.

d. In order to determine suitable conditions for the polymerization of 2,2-dinitrobutyl acrylate in the presence of nitro condensation polymers, exploratory experiments were conducted using various catalysts and promoters in the presence of stabilizers such as those used with nitrocellulose.

e. Table III gives the percent of yield and relative viscosity for various catalyst, promoter, and stabilizer combinations. It appears that the addition of both stabilizers is beneficial, with respect to both yield and molecular weight. The polymerizations were conducted at 45°C under a nitrogen atmosphere.

TABLE III

POLYMERIZATION OF 2,2-DINITROBUTYL ACRYLATE WITH VARIOUS CATALYSTS AND STABILIZERS

Catalyst	Promoter	Stabilizer	Yield, %	η_r (1% in Acetone)
1/4% MAKP[a]	—	--	89	2.45
1/4% Bz_2O_2[b]	0.1% DMA[c]	--	78	1.72
1/4% Bz_2O_2[b]	0.1% DMA[c]	1/4% MNA[d]	82	2.08
1/4% Bz_2O_2[b]	0.1% DMA[c]	1/4% + 1/4% Sn[e]	91	2.54

[a] MAKP is methyl amyl ketone peroxide.

[b] Bz_2O_2 is benzoyl peroxide.

[c] DMA is dimethyl aniline.

[d] MNA is N-methyl p-nitroaniline.

[e] Sn is dibutyl tin dilaurate.

f. Experimental

The procedure for polymerizing the samples of DNBA with various catalysts, accelerators, and stabilizers is that described in Aerojet Report No. 663, p. 57.

B. ADDITION AND CONDENSATION POLYMERS

1. Polyurethanes

a. Chelated-Metal Compounds as Catalysts for Polyurethane Formation

(1) Previous experiments have shown that vanadyl acetylacetonate and chromium acetylacetonate are superior to boron trifluoride as catalysts for nitropolyurethane formation.* Ferric acetylacetonate** has now been studied in conjunction with the polyurethane I-J system. Table IV lists the observed rate constants for the reaction of 3,3-dinitro-1,5-pentane diisocyanate with 2-nitro-2-methyl-1,3-propanediol, using various catalysts.

TABLE IV

RATE CONSTANTS FOR CATALYZED POLYURETHANE I-J

Catalyst	Monomer Concentrations Equiv./liter	Catalyst Concentration mole/liter	K_{50°, liter/equiv. hr
Ferric acetylacetonate	0.940	1×10^{-5}	3.6
Ferric acetylacetonate	0.940	1×10^{-4}	26
Vanadyl acetylacetonate	0.910	1×10^{-4}	9.7×10^{-1}
None	2.37	--	2.3×10^{-3}*

*Aerojet Report No. 590, p. 27.

(2) The ferric acetylacetonate is by far the most effective catalyst for nitropolyurethane formation. In addition to preparations of polyurethane I-J, ferric acetylacetonate has proved effective as catalyst in the polyurethane I-A and I-H systems.

*Aerojet Report No. 663, p. 13.

**Ibid., p. 79.

(3) Experimental

The monomers in equivalence were dissolved in anhydrous dioxan. The appropriate amount of catalyst was added to the monomer solution at zero time and samples were periodically removed for (-NCO) analysis by the standard procedure.* Tables V and VI list the observed data, which are shown graphically in Figures 3, 4. and 5.

TABLE V

FERRIC-ACETYLACETONATE-CATALYZED POLYURETHANE I-J;
RATE IN DIOXAN SOLUTION AT 50°C

(Original concentration 0.940 equiv./liter (-NCO) and (-OH); ferric acetylacetonate concentration 10^{-5} mole/liter)

Elapsed Time, hr	Observed DP
0.25	1.87
0.75	3.70
1.25	5.20
1.75	7.25
3.00	11.0
4.00	14.5
5.00	18.0

$$K_{50^\circ} = \frac{3.40}{0.940} = 3.62 \text{ liter/equiv. hr}$$

(Original concentration 0.940 equiv./liter (-NCO) and (-OH); ferric acetylacetonate concentration 10^{-4} mole/liter)

Elapsed Time, hr	Observed DP
0.25	20
0.75	29
1.25	35
1.75	54
3.00	63
4.00	94
5.00	125

$$K_{50^\circ} = \frac{2.49}{0.940} = 26.4 \text{ liter/equiv. hr}$$

TABLE VI

VANADYL-ACETYLACETONATE-CATALYZED POLYURETHANE I-J;
RATE IN DIOXAN SOLUTION AT 50°C

(Original concentration 0.910 equiv./liter (-NCO) and (-OH); vanadyl acetylacetonate concentration 10^{-4} mole/liter)

Elapsed Time, hr	Observed DP
0.5	1.43
1.0	2.06
1.5	2.40
2.0	2.63

$$K_{50^\circ} = \frac{0.88}{0.91} = 0.97 \text{ liter/equiv. hr}$$

*Aerojet Report No. 638, p. 25.

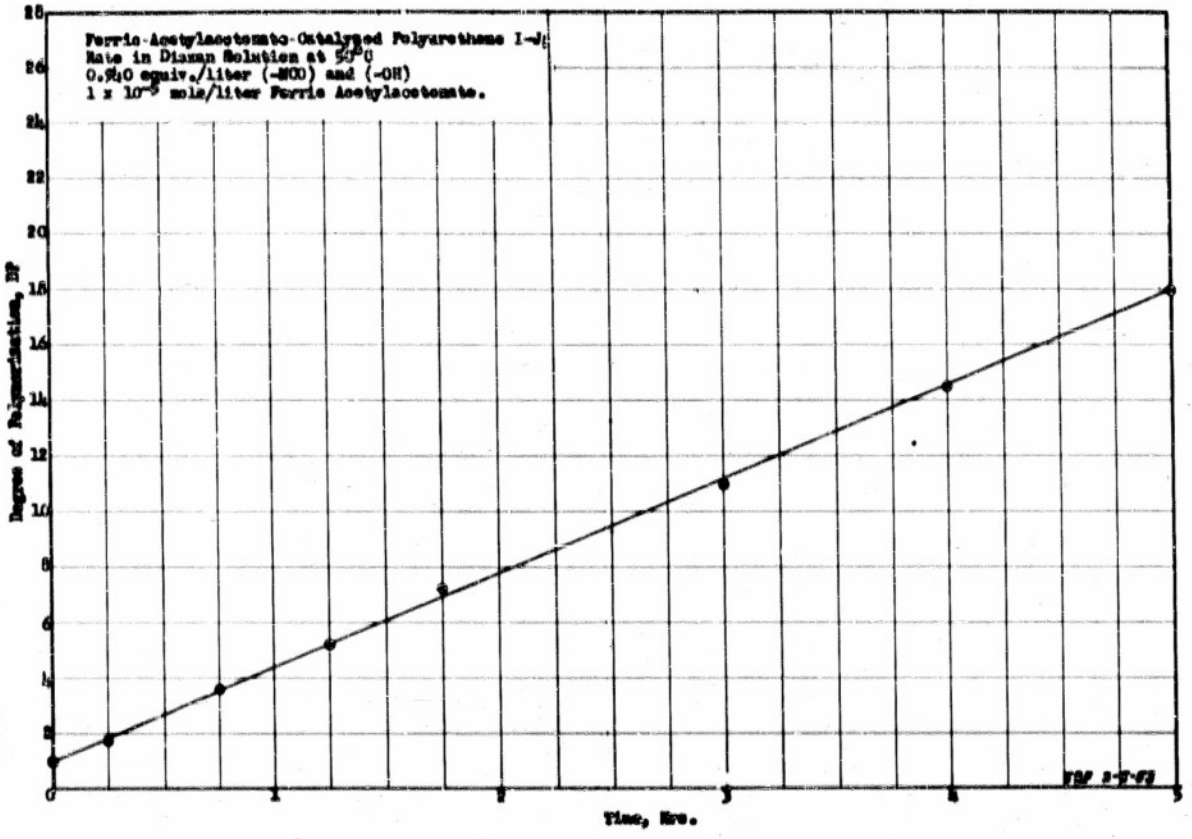

Figure 3

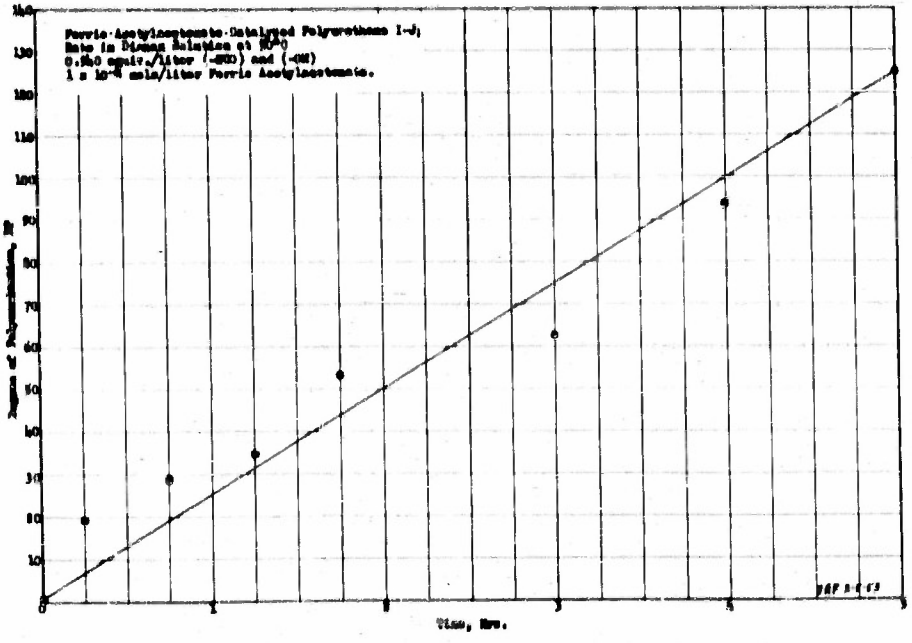

Figure 4

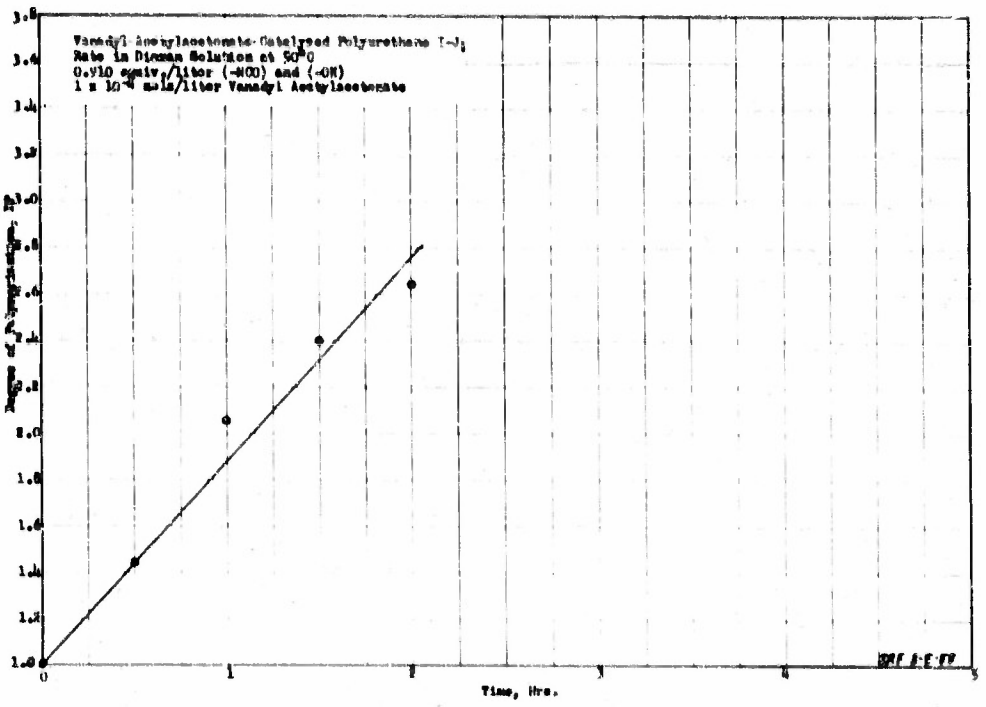

Figure 5

b. Stability Studies

(1) Introduction

In continuation of the stability studies on post-nitrated polyurethanes, work during this period has been focused on homogeneous washing of solutions of polyurethane I-AN with urea. Whereas satisfactory thermal stabilities have been obtained, severe degradation was noted, as in previous work. Thus, using the technique of homogeneous washing, the problem of thermal stability has been solved; but another problem, that of polymer degradation, has been introduced. In view of other stability studies, using a warm sodium bicarbonate wash to remove nitric acid, the entire approach of homogeneous washing is being abandoned. A vacuum steam distillation of unstable I-AN was also attempted; but under the conditions used, stable polymer was not obtained.

(2) Urea Stabilization of Polyurethane I-AN in Dioxan Solution

(a) Experimental

Twenty-five ml of absolute dioxan was added to 1 g of polyurethane I-AN (JKE-117-c, $\eta_r^{1\%} = 1.13$, $stab_{65.5^\circ} = 1$ min). One ml of a saturated methanol solution of urea was added to this solution, and urea

immediately crystallized from the dioxan solution. After the urea was filtered off, the solution was poured into water in a blendor, precipitating the polymer. The polymer was water-washed and vacuum dried. In order to increase the activity of urea in the dioxan solution of polymer, the above reaction was repeated, maintaining the temperature of the dioxan solution for 10 min at 40°C. Relative viscosities were determined in acetone solution at 1.000 g/100 ml at 25°C, and thermal stabilities were determined on 1.3-g samples at 65.5°C, to starch-iodide coloration. The results are presented in Table VII.

TABLE VII

UREA WASHING OF POLYURETHANE I-AN IN DIOXAN SOLUTION

Run	Conditions	$Stab_{65.5°}$	$\eta_r^{1\%}$
1	Urea-MeOH added at room temp; ppt. immediately	5-min, heavy failure	1.10
2	Urea-MeOH added at 40°C; ppt. after 10 min at 40°C	Trace in 10 min; no further coloration in 2 hr	1.07

(b) Conclusions

Urea appears to be combining with nitric acid. The low solubility of urea in dioxan prevents quantitative removal of acid from the system. Degradation is significant, particularly at the higher temperature.

(3) Urea Stabilization of Polyurethane I-AN in Dimethylformamide Solution

(a) Experimental

Six g of polyurethane I-AN (JKE-122, $\eta_r^{2\%} = 1.60$, $stab_{65.5°} = 3$ min) was added to 100 ml of technical dimethylformamide, and after being dissolved the solution was divided into two portions. Five ml of water was added to one portion, and after 10 min, the polymer was precipitated in water, washed, and vacuum dried. Ten ml of a saturated methanol solution of urea was added to the other portion and after 10 min, the polymer was precipitated in water, washed, and vacuum dried. Relative viscosities and thermal stabilities were determined under standard conditions. The results are presented in Table VIII.

TABLE VIII

UREA WASHING OF POLYURETHANE I-AN IN DIMETHYLFORMAMIDE SOLUTION

Run	Conditions	$Stab_{65.5^\circ}$	$\eta_r^{2\%}$
1	I-AN diss. in DMF; H_2O added	Trace in 5 min; no further in 3 hr	1.19
2	I-AN diss. in DMF; urea-MeOH added	No failure in 3 hr	1.11

(b) Conclusions

Here again urea has effected high stability (η_r = 1.60 drops to η_r = 1.11). It must be concluded that solutions of polyurethane I-AN are extremely sensitive to bases (urea $K_B = 1.5 \times 10^{-14}$), and any stabilization procedure which obviates a solution reaction is to be desired.

(4) Vacuum Steam Distillation of Unstable Polyurethane I-AN

(a) Introduction

In an attempt to remove occluded nitric acid from a freshly precipitated sample of polyurethane I-AN, a vacuum steam distillation of the unstable polymer was attempted, in the hope of either leaching out the acid or distilling it from the system. Under the conditions used, no stability was effected; however, there was an indication that more severe conditions might be effective.

(b) Experimental

A 3-liter steam-distillation flask was charged with 40 g of polyurethane I-AN (JKE-117, $\eta_r^{1\%}$ = 1.17, $stab_{65.5^\circ}$ = 3 min) and about 1 liter distilled water, and the system was vacuum steam distilled for 1.5 hr at 20°C. Four hundred ml of distillate was collected. One-half the charge was removed, and the ramainder was further distilled for 30 min at 40°C; 250 ml of distillate was collected. Measurements of pH, using a Beckman pH meter, were made on the several distillate and pot fractions. The polymers were washed and vacuum dried. Relative-viscosity determinations were made in acetone solution at 1.000 g/100 ml at 25°C, and thermal stabilities were determined on 1.3-g samples at 65.5°C, to starch-iodide coloration. The results are shown in Table IX.

TABLE IX

VACUUM STEAM DISTILLATION OF UNSTABLE POLYURETHANE I-AN

Run	Steam Dist. Conditions	pH Distillate	pH Polymer Slurry	$Stab_{65.5°}$	$\eta_r^{1\%}$
1	Control; no steam dist.	—	5.0	3 min	1.17
2	1.5 hr at 20°C	5.0	4.0	2 min	1.13
3	1.5 hr at 20°C 0.5 hr at 40°C	5.0	2.3	1 min	1.13

(c) Conclusions

Under the conditions of vacuum steam-distillation used, nitric acid was not completely removed. At the higher temperature, the rate of removal of acid appears to be faster. Nitric acid, under these conditions, is not distilled from the reaction flask. A small amount of degradation appears to have taken place during the steam distillation.

(5) Stabilization of Polyurethane I-JN Using a Warm Sodium Bicarbonate Wash

(a) Attempts were made to remove the nitric acid with dilute sodium bicarbonate solution. Polyurethane I-J (JRF-191-A, η_r = 2.52, 1% in acetone) was treated with distilled 100% nitric acid for 20 min at 0°C, then precipitated by pouring into ice and water in a Waring Blendor. One portion (JRF-193-A-1) was agitated in the Blendor for 15 min at 25°C with dilute sodium bicarbonate; the other portion (JRF-193-B-1) was agitated in the Blendor 15 min at 50°C. Both were then washed thoroughly with water and dried.

(JRF-193-A-1) 25°C, $stab_{65.5°}$ = 3 min; η_r = 2.41, 2% in acetone

(JRF-193-B-1) 50°C, $stab_{65.5°}$ = 20 min; η_r = 2.53, 2% in acetone

A larger amount (25 g) of polyurethane I-J (JRF-191-B-2, η_r = 5.44, 2% in acetone), was treated with distilled 100% nitric acid at 0°C. The material dissolved slowly, requiring one hour for complete solution. After precipitation into ice and water, the polymer was stirred with dilute sodium bicarbonate for 10 min at 50°C, then water-washed and dried. For JRF-193, η_r = 1.57, 2% in acetone; $stab_{65.5°C}$ = 20 min. Preparation JRF-193 was again treated with dilute sodium bicarbonate. The results are listed in Table X.

TABLE X

STABILIZATION OF POLYURETHANE I-JN USING A WARM SODIUM BICARBONATE WASH

Identification	$NaHCO_3$ Treatment		KI-Starch Stability, 65.5°C	η_r*
	Time	Temperature		
(JRF-193-A)	15 min	65°C	45 min	1.69
(JRF-193-B)	1 hr	50-65°C	80 min	1.71
(JRF-193-C)	2 hr	50-65°C	> 4 hr	1.62

*2% in acetone.

(b) Conclusions

Thorough washing with dilute sodium bicarbonate solution at 50 to 65°C effectively removes the nitric acid, as evidenced by the increased thermal stability. A small amount of degradation occurs during the washing. However, it appears that extensive degradation occurs during the nitration. This will be investigated further.

c. Further Work on Polyurethanes Previously Described

(1) Introduction

The chelated-metal catalysts have made possible the preparation of high-molecular-weight polyurethanes having desirable physical properties.* Since these catalysts behave differently from the boron trifluoride previously used, optimum reaction conditions must again be determined for each of the polyurethanes previously described. Other objectives include elucidation of the catalyst mechanism, reproducibility of product, and the cause of product insolubility observed in some preparations. The more important variables are concentration of monomers and catalyst, solvent, time, temperature, order of mixing the reactants, monomer ratio, and the procedure used for working up the product.

(2) Polyurethane I-J: 3,3-Dinitro-1,5-pentane Diisocyanate and 2-Nitro-2-methyl-1,3-propanediol

(a) Previous work has shown that monomer concentration markedly effects the molecular weight of the product.** In the polyurethane I-J system, most of the preparations have been carried out at a concentration of one mole of each monomer per liter of dioxan solution.

*Aerojet Report No. 663, p. 29.

**Ibid., p. 31.

This corresponds to 34.2 wt% solids. At this concentration the solution can be stirred and the solution viscosity can be measured while the polymerization is in progress. Small runs were made at higher concentrations both at monomer equivalence and with the diisocyanate in excess by one percent. The technique employed can be used only for small preparations, in which the heat of reaction can be readily removed. The required amount of dioxan containing the dissolved catalyst was added to the monomers in a 125-ml glass-stoppered Erlenmeyer flask. The diisocyanate dissolved rapidly, followed more slowly by the diol. After several minutes the heat of reaction resulted in a rapid temperature rise and a rapid dissolution of the remaining diol. The solution simultaneously became too thick to stir. Table XI summarizes the results.

(b) The cause of insolubility in the more concentrated solutions is not definitely known. It may be due to reaction of (-NCO) with urethane linkages under the influence of high temperature and the very active ferric acetylacetonate catalyst, inasmuch as the diisocyanate was in excess until the diol had completely dissolved. The work was repeated with the same monomers, adding the diisocyanate portionwise to the diol solution containing catalyst, and keeping the temperature in the range from 30 to 40°C during the addition. Table XII summarizes the results. In all cases the product was completely soluble in dioxan.

(c) Conclusions

Higher monomer concentrations are desirable, but the temperature must be carefully controlled during the initial mixing of the monomers to prevent the formation of insoluble product.

(d) Another variable is the procedure used for working up the product. If an equilibrium between low- and high-molecular-weight product exists, it may be unfavorably shifted when the viscous solution is diluted before precipitating the polymer, especially in the presence of very active catalysts. Table XIII lists variations in the work-up procedure and their effect on the relative viscosity of the finished polymer. It is concluded that dilution with dioxan at room temperature, followed by precipitation, does not adversely affect the relative viscosity of the product. At higher temperatures, the relative viscosity of the product slowly decreases. Treatment with dilute HCl solution effectively removes the ferric acetylacetonate catalyst but causes some degradation.

TABLE XI

POLYURETHANE I-J PREPARATIONS IN DIOXAN

No.	Eq. Diisocy.	Eq. Diol	Wt%	Ferric Acetylacetonate Catalyst* Concentration	Reaction Time, hr	Reaction Temp, °C	Maximum Temp During Mixing, °C	η_r **
JRF-199	0.0440	0.0440	34.2	5×10^{-4}	138	50	50	2.42
JRF-200	0.0420	0.0420	50.0	5×10^{-4}	138	50	70	2.16 Sol. portion
JRF-201	0.0650	0.0650	60.0	5×10^{-4}	138	50	80	— Insol.
JRF-202	0.0452	0.0447	34.2	5×10^{-4}	144	50	50	2.48
JRF-203	0.0472	0.0467	50.0	5×10^{-4}	144	50	70	2.38 Sol. portion
JRF-204	0.0512	0.0507	60.0	5×10^{-4}	144	50	80	— Insol.

*Moles catalyst per equivalent (-OH).

**1% in acetone.

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TABLE XII

EFFECT OF MONOMER CONCENTRATION IN POLYURETHANE I-J SYSTEM

No.	Eq. Diisocy.	Diol	Wt%	Ferric Acetylacetonate Catalyst Concentration*	Reaction Time, hr	Reaction Temp, °C	Maximum Temp During Mixing, °C	η_r**
JRF-197	0.534	0.532	34.2	5×10^{-4}	191	50	50	1.68
JRF-198	0.523	0.522	34.2	5×10^{-4}	171	50	50	1.67
JRF-205	0.538	0.535	50	5×10^{-4}	164	50	40	1.82
JRF-207	0.525	0.524	50	5×10^{-4}	115	50	40	1.92
JRF-206	0.537	0.534	60	5×10^{-4}	163	50	40	1.93

*Moles catalyst per equivalent (-OH).

**1% in acetone.

TABLE XIII

VARIATIONS IN WORK-UP OF POLYURETHANE I-J

No.	Work-Up Procedure	η_r (1% in Acetone)
JRF-195-C	Diluted at 25°C with dioxan and precipitated within 15 min	1.87
JRF-195-D	34% Solution precipitated without diluting	1.86
JRF-195-E	Diluted with dioxan and let stand 5 days at 25°C before precipitating	1.88
JRF-195-F	Diluted with dioxan containing a small amount of bromine, let stand 5 days at 25°C before precipitating	1.89
JRF-195-G	Diluted with dioxan plus several drops of water, let stand 5 days at 25°C before precipitating	1.89
JRF-195-J	Diluted with dioxan plus several drops of 2N HCl, and precipitated within 15 min; pure white polymer	1.84
JRF-197-B	Diluted with dioxan and ferric acetylacetonate; held at 50°C for 200 hr before precipitating	1.52
JRF-197-C	Diluted with dioxan and 10 equiv. % 3,3-dinitro-1,5-pentane diisocyanate; held at 50°C for 200 hr before precipitating	1.33
JRF-197-D	Diluted with dioxan and 10 equiv. % 2-nitro-2-methyl-1,3-propanediol; held at 50°C for 200 hr before precipitating	1.48
JRF-197-E	Control for 197 series; held at 50°C 200 hr, then diluted and precipitated	1.61

(3) Polyurethane I-A: 3,3-Dinitro-1,5-pentane Diisocyanate and 2,2-Dinitro-1,3-propanediol

(a) Using the new chelated-metal catalysts in the I-A system, reaction times have been materially reduced, and molecular weights have been consistently high (with diisocyanate adjustment). Of the three metal catalysts recently obtained, the iron salt was selected for study, based on the results of previously described work in which the high activity of the iron catalyst was demonstrated.* With the purpose of preparing large quantities of stable, postnitrated polyurethanes for the formulation program, recent preparations of polyurethane I-A have been moderately large. In each case an attempt has been made, by changing the appropriate variables, to determine the optimum preparative conditions for this system. These data have been summarized in Table XIV.

*Aerojet Report No. 663, p. 22.

TABLE XIV

POLYURETHANE I-A PREPARATIONS USING FERRIC ACETYLACETONATE CATALYST

Weight Reaction				% I.A.A. (moles catalyst per equiv. diiso. x 100)	Monomer Ratio	Order of Addition	Yield %	$\eta_r^{2\%}$	$Stab_{65.5^\circ C}$
JKE No.	Prepn. g	Time hr	Wt% Monom.						
111	67	97	50	0.1	2% Excess diiso.	Cat $\longrightarrow$ Ol+Iso[1]	96	1.96	2.5 hr
115	205	260	50	0.05	1.25% Excess diiso.	Iso $\longrightarrow$ Ol+Iso+Cat[2,3] (58%) (42%)	100	2.16[4]	>4 hr
118	156	306	50	0.05	0.5% Excess diiso.	Iso $\xrightarrow{50-60^\circ C}$ Ol+Cat	104	2.00	Trace 20 min
119	87	123	50	0.05	0.5% Excess diiso.	Iso $\xrightarrow{25-30^\circ C}$ Ol+Cat	103	1.98	Trace 10 min
121	146	66	70	0.05	Equiv.	Iso $\xrightarrow{60^\circ C}$ Ol+Cat	101	1.67	40 min
123	213	42	70	0.05	1% Excess Diiso.	Iso $\xrightarrow{60^\circ C}$ Ol+Cat	98	2.22	4 hr

[1] Catalyst was added to the dioxan solution of the diol and diisocyanate.

[2] 58% of the diisocyanate was added to solution of catalyst plus diol plus remaining 42% of diisocyanate.

[3] Since this condensation, when catalyzed by the iron salt, is extremely exothermic, one monomer must be added dropwise in order to control the reaction.

[4] This relative viscosity corresponds to a molecular weight of 32,000 determined osmometrically.

(b) Experimental

Most experimental conditions are given in Table XIV. In all cases the reaction solvent was absolute dioxan, and the reactions were followed by periodic measurements of solution viscosity, and were terminated when the viscosity vs time curve leveled off. The work-up procedure was the same in each case: The viscous polymer solutions were diluted with dioxan to about 10 wt%, filtered, and precipitated dropwise into ice-water in a Waring Blendor, followed by further Blendor washing in ice-water, and last, vacuum drying. The extreme difficulty in completely removing the solvent from these high-molecular-weight polyurethanes is shown by the yields, some of which are greater than 100%.

(c) A study of the effect of monomer concentration on molecular weight in the I-A system was made. In other polyurethane systems, I-H and I-O, a dependence of molecular weight on monomer concentration has been noted.# Using the ferric acetylacetonate catalyst in the I-A system, it was of importance to determine the effect of monomer concentration. Accordingly, five polymer runs were made, in which the concentration was varied from 1 wt% to 80 wt%. A linear relationship was found between monomer concentration and relative viscosity (see Figure 6).

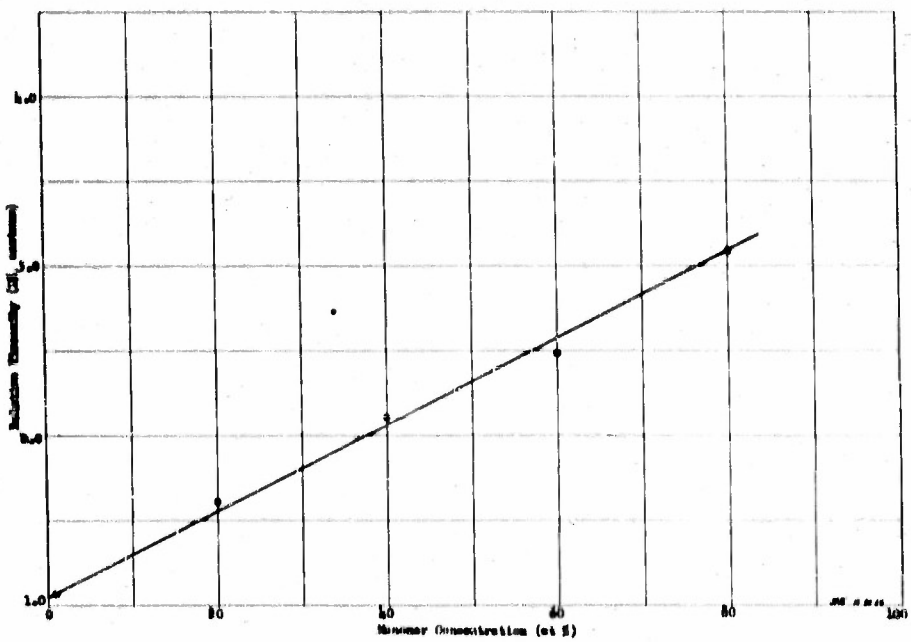

Figure 6

Polyurethane I-A
Effect of Monomer Concentration on Molecular Weight

#See Aerojet Report No. 638, pp. 27, 35.

(d) Experimental

The diol was weighed into a glass-stoppered, 125-ml Erlenmeyer flask, followed by the calculated amount of diisocyanate to give 1% excess diisocyanate, and sufficient absolute dioxan to give the desired weight percent of monomers. The total weight of monomers was about 10 grams. After complete dissolution of monomers, ferric acetylacetonate was added in an amount giving 0.05% of diisocyanate equivalents present. In the 60 and 80 wt% runs, 30 to 60 seconds after adding the catalyst, the reaction solutions were boiling inside the stoppered flasks. The 40 wt% run warmed to about 60°C, and the 20 wt% run, to about 45°C. The 1 wt% run showed no perceptible temperature rise. After the initial heat of polymerization had been spent, the reaction flasks were placed in a 50°C bath, where they remained for 145 hours. The polymers were worked up by diluting in dioxan, filtering, precipitation into water, water-washing in a Blendor, and vacuum drying. Relative viscosities were determined at 2% in acetone. The results are presented in Table XV.

TABLE XV

EFFECT OF MONOMER CONCENTRATION ON MOLECULAR WEIGHT IN I-A SYSTEM

Run No.	Monomer Conc. Wt%	Physical State of Reaction Soln. at Completion	Relative Viscosity
JKE-127	80	Hard solid; small amt. of insol. gel after dissolving in dioxan	3.08
JKE-128	60	Semi-solid	2.48
JKE-129	40	Extremely viscous liquid	2.11
JKE-130	20	Viscous liquid	1.61
JKE-131	1	Liquid	1.06

(e) A study of the effect of catalyst concentration on molecular weight in the I-A system was made. In using ferric acetylacetonate as a catalyst for polyurethane formation in the I-A system, only catalytic amounts have been necessary to give a very fast rate to a high DP. It was desired to establish a more quantitative relation between catalyst concentration and molecular weight as measured by relative viscosity. Three polymerization runs in which the catalyst concentration was varied from 0.01 to 1% showed that the lower concentrations of catalyst led to significantly higher molecular weights. Data are given in Table XVI.

TABLE XVI

EFFECT OF CATALYST CONCENTRATION ON MOLECULAR WEIGHT IN I-A SYSTEM

Run No.	Cat. Conc.*	Time to Maximum Initial Temp	Rel. Viscosity
JKE-133	0.01%	5 min	2.34
JKE-134	0.10%	2 min	2.01
JKE-135	1.00%	20 sec	1.42

*(Moles catalyst per equivalent diisocyanate) x 10^2.

(f) Experimental

The diol was weighed into a glass-stoppered, 125-ml Erlenmeyer flask, followed by the calculated amount of diisocyanate to give 1% excess diisocyanate, and sufficient absolute dioxan to give 50 wt% solutions. The total weight of monomers was about 10 g. The calculated amount of ferric acetylacetonate was added to give the desired catalyst concentration. In each of the three runs the reaction temperature rose to 60 to 70°C within minutes after adding the catalyst, and then cooled slowly. The reaction flasks were placed in a 50°C bath for 210 hours. Precipitation of the polymer was effected in ice water in a Waring Blendor, followed by vacuum drying. Relative viscosities were determined at 2% in acetone.

(g) In continuation of the study of the important variables in the I-A system, the order of addition of monomers has been investigated. It was found that significantly higher molecular weights were obtained when the diol was added to the diisocyanate, than when the order of addition was reversed. Two hypotheses are tenable: (1) conditions for isocyanate-urethane cross-linking are ideal when diol is added to diisocyanate; and (2) during the addition of the diol, the diisocyanate, being in the presence of catalyst, can self-polymerize. Either effect gives rise to a higher viscosity. Further work will determine which of the two theories best explains the facts.

(h) Experimental: Diisocyanate Added to Diol

A solution of the diisocyanate in absolute dioxan was added dropwise to a dioxan solution of an equivalent amount of diol over a period of 1 hour. The total monomer weight was 94 g, and the ultimate monomer concentration was 50 wt%. Ferric acetylacetonate was added to the diol

prior to diisocyanate addition, giving a concentration of 0.05% (5×10^{-4} mole catalyst per equivalent diol). At the completion of the addition of diisocyanate, the reaction temperature was about 60°C. The reaction vessel was placed in a 50°C bath, and the polymerization was followed by measurements of the solution viscosity. The equivalence of monomers was subsequently adjusted by the addition, in three portions, of a total of 1.35% by weight excess diisocyanate. The reaction was terminated in 195 hours, when the viscosity vs time curve showed no tendency to rise further. The polymer solution was worked up by diluting with dioxan, filtering, precipitation in water, and vacuum drying. The relative viscosity of a 2% solution in acetone was 2.09.

(i) Diol Added to Diisocyanate

The above-described experiment was duplicated, using the same monomers, with the following exceptions: The diol was added portionwise to the diisocyanate, the total monomer weight was 151 g, and the required 1.35% excess diisocyanate was added at the beginning. Within 20 hours at 50°C, the solution viscosity had reached a constant value which was far below the final value in the first experiment, indicating that isocyanate had been consumed in some side reaction. The addition of another 1% diisocyanate to the reaction solution immediately caused a rapid rise in the viscosity vs time curve. When this curve leveled off after a total reaction time of 408 hours, the reaction was terminated, and the polymer was worked up as described above. The relative viscosity of a 2% solution in acetone was 2.57.

(j) Recently, some doubt has arisen with respect to accuracy and sensitivity of the solution viscosity vs time curves normally used to follow polymerization reactions. In the experiment described below a typical polyurethane I-A run was made, and the reaction was followed by determinations of solution viscosity and also of relative viscosity (determined on samples precipitated at appropriate intervals). A close correspondence between the two viscosity vs time curves (see Figure 7) establishes the validity of the solution-viscosity measurements. In addition, the arbitrary units used in the solution-viscosity measurements have been referred to an absolute system.

(k) Experimental (JKE-124)

To 0.228 mole of diol in 40 ml of absolute dioxan in a 500-ml resin flask was added dropwise 0.228 mole of diisocyanate in 50 ml of absolute dioxan. The ultimate monomer concentration was 50 wt%. At the outset, 0.228 millimole of ferric acetylacetonate was present with the diol. The heat of polymerization accumulated rapidly, and the rate of addition of diisocyanate was so adjusted that the reaction temperature never rose above 60°C. One hour was required for the addition of all of the diisocyanate solution. The reaction vessel was placed in a 50°C bath immediately after the diisocyanate addition. The solution viscosity was measured by determining the efflux time of the solution between two marks in 6-mm Pyrex tubing 1 cm apart, the lower one being 1 cm above the surface of the solution, and the end of the tubing being 1 cm below the surface. At appropriate intervals, small samples

were removed, diluted with dioxan, precipitated in water, washed, and vacuum-dried. The relative viscosities of these samples were determined in a modified Ostwald viscosimeter in acetone at 25°C, at a concentration of 2.000 g/100 ml. At three points during the reaction additional diisocyanate was added (as indicated in Figure 7) by vigorously stirring the monomer crystals into the reaction solution. The reaction was terminated after 195 hr, and the work-up was identical to that for the small portions.

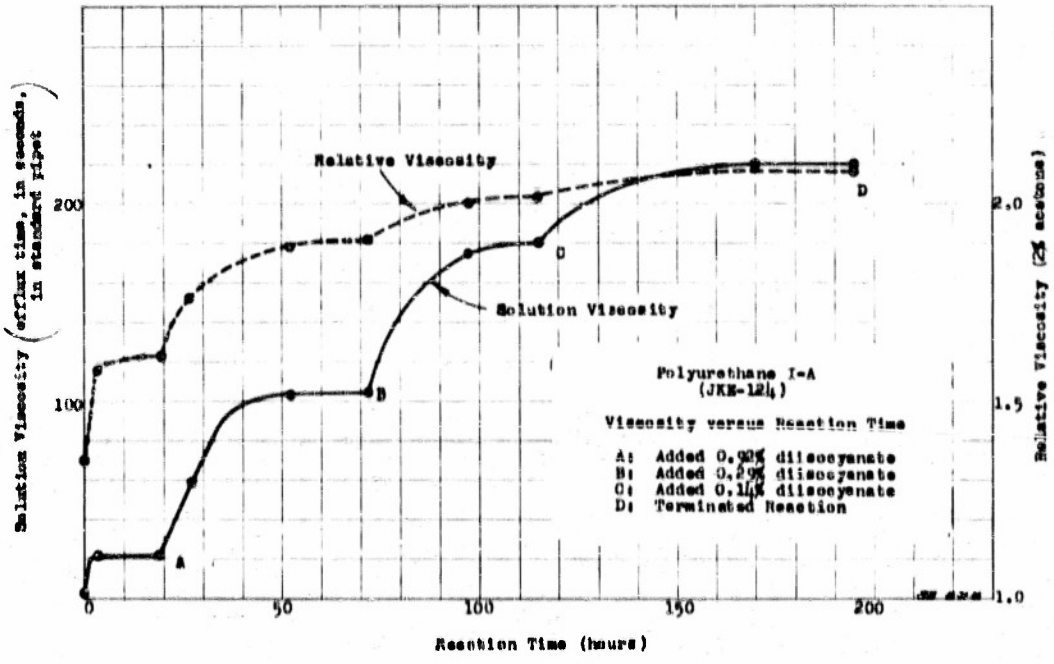

Figure 7

(4) Preparation of Polyurethane I-H: 3,3-Dinitro-1,5-pentane Diisocyanate and 5,5,5-Trinitro-1,2-pentanediol

(a) Introduction

The marked success that has been achieved in obtaining high molecular weights in the I-A and I-J systems, using the iron catalyst, had led to a program of reappraisal of many old polymer systems, for which only low molecular weights had been obtained when boron trifluoride etherate was used as catalyst.

(b) Experimental

To 119.50 g diol in a 500-ml resin flask was added 171 ml absolute dioxan and 29.09 g (23%) of diisocyanate. Iron

catalyst was introduced by the addition of 10 ml of a dioxan solution containing 177 mg of catalyst (0.5%). Immediate warming of the reaction solution was observed, and within 10 minutes the temperature was at 50°C. The remaining diisocyanate, 95.05 g (77%), was dissolved in 50 ml dioxan in a dropping funnel, and added dropwise to the diol solution at a rate which maintained the temperature between 45 and 55°C. The ultimate monomer concentration was 50 wt%. After all the diisocyanate was added, the reaction flask was placed in a 50°C bath, and the polymerization was followed to completion in 258 hours by solution-viscosity measurements. The viscous polymer mass was diluted with dioxan, filtered, precipitated in water, and vacuum dried. A fibrous, tan-colored polymer was obtained in 99% yield. The relative viscosity was 2.02 (2% in acetone) and the thermal stability was 10 min (starch-iodide at 65.5°C).

III. TECHNICAL PROGRESS: PHYSICAL STUDIES

A. MOLECULAR WEIGHT DETERMINED BY OSMOMETRY

1. General

With the use of iron acetylacetonate catalysts for the polyurethane condensation, polymers of relatively high molecular weight are being obtained. These higher polymers require measurement of molecular weight by the osmometric technique, which heretofore has not been very reliable for nitropolymers, because of the tendency of the lower-molecular-weight fractions to diffuse through the membrane. During the past quarter various other sources of error in the method were resolved, and attempts were made to evaluate the molecular weights of some of the high-molecular-weight preparations. The results indicate that diffusion of the low-molecular-weight fractions is still the main problem.

2. Temperature-Gradient Error

The structure of the Zimm-Myerson osmometer is such that the apparatus can function as a very sensitive thermometer if it is subjected to changing temperatures. The large cubical coefficient of expansion of acetone and the large volume of the osmometer cell relative to the volume of the capillary tube produce this sensitivity. If it is assumed that diffusion of acetone through the membrane is negligibly slow in comparison with the rate of expansion or contraction of acetone in response to changing temperature, the change in height in the osmotic-pressure capillary resulting from a 0.1°C change in temperature would be about 2.1 cm. The osmometers are mounted in a mercury-thermoregulated, constant-temperature bath, reputedly accurate to 0.01°C. However, random fluctuations in the osmotic capillary heights suggestive of changing temperature were observed, and it was believed that inadequate stirring of the water in the bath could account for these fluctuations. The constant-temperature bath was equipped with a more efficient stirrer, and the stability of the osmometer capillary heights was observed with pure acetone in the osmometer cells. With the improved stirrer, the capillary heights were perfectly stable, within the limit of accuracy of the reading, both with acetone and polymer solutions in the cells. Goldblum points out that temperature control is essential, not only to prevent the thermometric effect in the capillaries of the osmometers, but because the slope of the π/c vs c curve may be strongly dependent on temperature.*

*K. B. Goldblum, J. Phys. & Colloid Chem. 51, 474 (1947).

3. Surface-Tension Error

The capillary rise due to surface tension was measured in one of the osmometers for pure acetone, and for the most concentrated polymer solution used to date (polyurethane I-J, 0.016 g ml^{-1}). The values agreed within 0.1 cm (the limit of accuracy of the reading), so that it will be assumed in the future that the effect of concentration on surface tension is negligible. Hookway and Townsend also found this to be the case with solutions of polystyrene in various solvents.*

4. Density Error

The densities of four solutions of polyurethane I-J in acetone were determined. It was calculated that the maximum error resulting from using the density of acetone in calculating molecular weight instead of the density of the actual solution would be about 2% for the most concentrated polymer solution used to date. Accordingly, the actual densities of the solutions were used in all calculations.

5. Polyurethane I-J, Preparation 195-A

Molecular-weight runs were made on polymer I-J, preparation JRF-195-A, the polyurethane of 3,3-dinitro-1,5-pentane diisocyanate and 2-nitro-2-methyl-1,3-propanediol. Several runs were made at each concentration, with the results shown in Table XVII. The equation for osmotic pressures of dilute polymer solutions, derived from the Huggins-Flory equation for free energy of the solutions, as stated by Mark and Tobolsky in terms of concentration,** is

$$\frac{\pi}{c} = \frac{RT}{M_p} + \frac{RT}{V_o d_p^2}(1/2 - \mu)\, c$$

where

π = osmotic pressure, atm

c = concentration of solution, g ml^{-1}

R = the gas constant, 82.07 ml atm $mole^{-1}$ $^oK^{-1}$

T = the absolute temperature, ^oK

V_o = mole volume of solvent, ml $mole^{-1}$

d_p = density of the polymer, g ml^{-1}

μ = interaction index for solvent-polymer, indicative of the solvent power of the solvent for the solute

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*H. T. Hookway and R. Townsend, J. Chem. Soc., 3190 (August 1952).

**H. Mark and A. V. Tobolsky, Physical Chemistry of High Polymeric Systems (Interscience Publishers, New York, 1950), p. 262.

TABLE XVII

DETERMINATIONS OF OSMOMETRIC MOLECULAR WEIGHT FOR VARIOUS POLYURETHANE PREPARATIONS

Number of Runs	c, Weighed,[1] g ml^{-1}	c, Corrected,[2] g ml^{-1}	h, cm[3]	Average Deviation[4]	Time to Maximum, hours[5]	π/c, ml atm g^{-1}	Leakage by Diffusion,[6] %
			Polyurethane I-J, JRF-195-A				
4	1.547×10^{-2}	1.447×10^{-2}	11.95	1.7%	22	0.636	5.8
5	1.015×10^{-2}	0.950×10^{-2}	7.06	2.1	30	0.568	7.9
4	0.714×10^{-2}	0.673×10^{-2}	4.62	2.6	22	0.521	6.7
4	0.447×10^{-2}	0.418×10^{-2}	2.59	10.0	26	0.470	5.2
			Polyurethane I-J, JRF-195-G				
5	1.011×10^{-2}	0.939×10^{-2}	7.22	2.1%	22	0.587	7.2
5	0.763×10^{-2}	0.708×10^{-2}	5.29	3.6	6	0.568	(7)
5	0.523×10^{-2}	0.486×10^{-2}	4.07	8.6	6	0.634	(7)
5	0.491×10^{-2}	0.456×10^{-2}	3.98	13.3	6	0.663	(7)
			Polyurethane I-A, JKS-128				
5	0.994×10^{-2}	0.967×10^{-2}	8.90	1.1%	46	0.702	2.7
5	1.256×10^{-2}	1.222×10^{-2}	12.60	2.4	6	0.787	2.7
4	0.757×10^{-2}	0.738×10^{-2}	6.91	13.1	6	0.713	2.4
5	0.499×10^{-2}	0.471×10^{-2}	4.98	6.4	6	0.803	5.7

(1) Concentration, g per ml acetone solution placed in the osmometer cell.

(2) Concentration, corrected for diffusion.

(3) Average osmotic pressure head, in cm of acetone solution.

(4) Average deviation from the mean in h.

(5) Elapsed time from filling of osmometers to attainment of maximum osmotic pressure.

(6) Weight percent of polymer subject to diffusion through the membrane.

(7) Not determined.

A plot of π/c vs c is shown in Figure 8. From the intercept of the extrapolated straight line the molecular weight was calculated to be 60,200, using the relationship

$$M_p = \frac{RT}{(\pi/c)_{c \longrightarrow o}}$$

The slope of the line, equal to

$$\frac{RT}{V_o dp^2} (1/2 - \mu)$$

was used to calculate μ, for which a value of 0.39 was obtained for the I-J—acetone system at 25°C. (The density of I-J is 1.467 g ml^{-1} and the mole volume of acetone is 74 ml.)

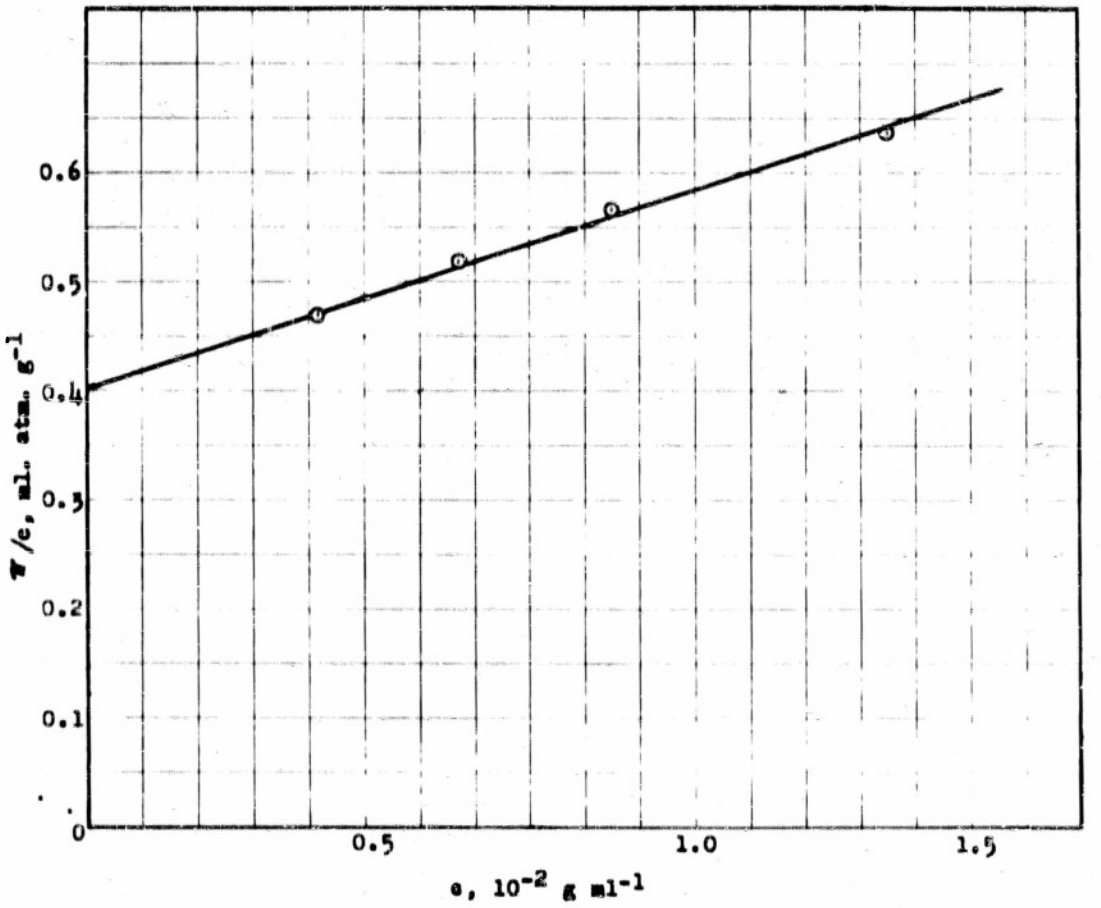

Figure 8

Molecular Weight of Polyurethane I-J (JRF-195-A)

6. Diffusion Error

It is to be noted in Table XVII that preparation JRF-195-A diffused through the membrane to an extent of 5 to 8% by weight. The amount of diffused polymer was measured by evaporating the acetone from the jacket surrounding the osmometer cell and weighing the non-volatile residue. The diffusion was manifested in the osmotic-pressure measurement by a continually decreasing pressure head after the maximum pressure was indicated. The diffusion error was measured as soon as possible after a decreasing pressure head was noted. The pressure maxima were determined by setting the osmotic columns at a low value and taking periodic readings until a falling meniscus was observed. In most cases the maximum was reached within 1-1/2 days, but the fall of the meniscus continued after the maximum, and there was no indication of a cessation of the diffusion in one run which was allowed to stand in the osmometer for a period of a week. The deviation of the diffusion measurements was quite large, up to values of 20% of the mean, because of the poor precision of measurement of such small quantities of polymer, but in no case was a complete absence of diffusion observed. In a quite thorough study of membrane permeabilities, Philipp and Bjork also noted that diffusion was observed in all cases and that the process proceeded continuously.* It would be desirable to know the average molecular weight of this diffused polymer, but such a measurement will be difficult because of the very low concentration.

7. Effect of Diffusion on Molecular Weight

a. An attempt was made to correct for the diffusion error as rigorously as possible in calculating the molecular weight of preparation JRF-195-A. As a basis for calculation, it was assumed that the concentration of polymer molecules which are small enough to be subject to diffusion through the membrane is the same in the inside of the osmometer cell as it is on the outside. The fact that the diffusion process does not come rapidly to an equilibrium tends to invalidate this assumption, but for lack of any other basis on which to work, it was assumed that the diffusion is sufficiently slow that the difference in concentration on the two sides of the membrane is negligibly small at the time at which the pressure head was read. The actual amounts of low-molecular-weight polymer on the inside and the outside of the osmometer cell will then be in proportion to the volumes of the liquid in the cell and in the osmometer jacket, which have the ratio of 1:13. Accordingly, the actual weights of diffused polymer obtained by the evaporation of the acetone in the jacket were multiplied by 14/13, to give the amount of polymer "subject to diffusion," from which the percentages reported in the eighth column of Table XVII were calculated. It was also assumed that the molecules subject to diffusion would have no effect on the osmotic pressure head developed in the osmometer, because their concentration would be the same on each side of the membrane. The pressure head would then be the osmotic pressure resulting from the large molecules retained in the cell, which are not subject to diffusion. The weight concentration of these large molecules (Column Three, Table XVII) was obtained from the original concentration (Column Two) by subtracting the amount subject to diffusion (Column Eight). The overall average diffusion for the runs on preparation JRF-195-A was 6.4%.

*H. J. Philipp and C. F. Bjork, J. Polymer Sci. 6, 383 (1951).

b. As a first approximation, calculations based on the above assumptions give a number-average molecular weight of 60,200 for the upper 93.6% (weight basis) molecular-weight fraction of preparation JRF-195-A. The unknown factor in this diffusion-error correction is the effect of the small molecules in the osmometer cell on the activities of the solvent and solute in the cell, solute in this case being defined as the polymer molecules which are not subject to diffusion. Because the average molecular weight, the molecular-weight distribution, and the actual number of the molecules subject to diffusion are all totally unknown at present, there is no manner in which their effect on activities can be estimated.

8. Rapid-Equilibrium-Approach Technique

a. In an attempt to minimize the diffusion error and to speed up the determination of osmometric molecular weight, a technique comparable to the rapid-equilibrium-approach* was used with polyurethane I-J, preparation JRF-195-C, and polyurethane IA, preparation JKE-128. For the first concentration with each of the preparations, the meniscus showing osmotic pressure was lowered manually immediately after the cell reached temperature equilibrium, to a value considerably below the expected osmotic-pressure head. (This was the technique used at all concentrations for polyurethane I-J, preparation JRF-195-A.) Observations of the rising pressure head were then taken periodically until a maximum was observed; the maximum occurred within 22 to 46 hours, as shown in Table XVII. For the second and subsequent concentrations on preparations JRF-195-C and JKE-128, the meniscus was elevated, after temperature equilibrium was attained, to a value just slightly below the expected maximum, calculated from the approximate osmotic pressure based on the result of the first concentration. The following points may be noted:

(1) The maxima occurred at six hours in all cases in which the rapid approach was used. (No readings were taken between the 6th and 22nd hours.)

(2) The diffusion was smaller for preparation JKE-128 than for preparation JRF-195-A.

(3) The deviation in osmotic pressure within individual runs at a given concentration (Column Five) is smaller with the long approaches to the maxima than with the rapid approaches.

(4) The plots of π/c vs c for the runs in which the rapid approach was used (Figures 9 and 10) do not give a rational relationship, whereas the runs in which the long approach was used (Figure 8) give a good linear plot.

*Aerojet Report No. 563 (31 December 1951), pp. 42-46.

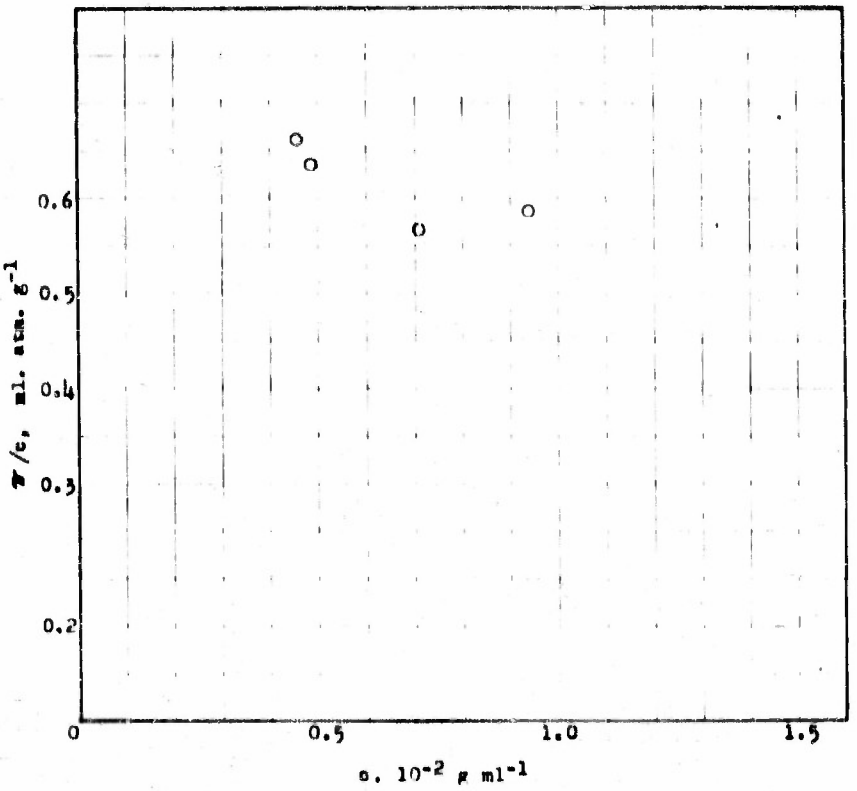

Figure 9

Molecular Weight of Polyurethane I-J (JRF-195-G)

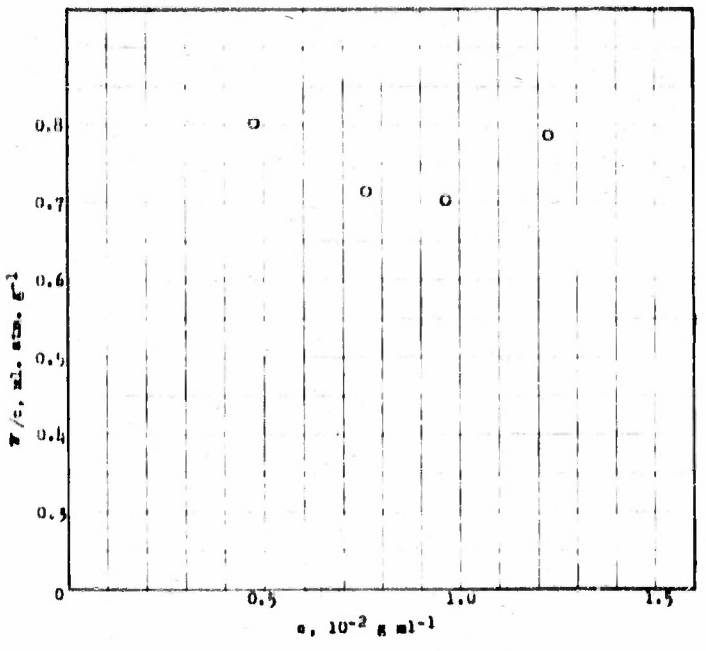

Figure 10

Molecular Weight of Polyurethane I-A (JKE-128)

b. Points (3) and (4) could be explained by assuming that the diffusion takes place most rapidly at the beginning of the determination and becomes progressively slower, although still in progress at the end of all of the runs shown in Table XVII. Under this condition the pressure equilibria (which depend on the diffusion) would be most unstable, and consequently most erratic, during the first few hours after the osmometer cells are filled. Consequently, the results would show better reproducibility, although not necessarily better accuracy, with the long approach to the maximum.

9. Molecular-Weight Distribution

The accuracy obtained with the long pressure-equilibrium approach will depend upon the molecular-weight distribution of the polymer. There are no data at present on molecular-weight distributions for nitropolymers developed in this laboratory. A report on fractionated nitrocellulose shows a quite uniform distribution of molecular weights between 20,000 and 150,000;* these fractions comprise about 25% of the total polymer. The remaining 75% exhibits molecular weights averaging 200,000; the overall number average determined on the unfractionated sample was 97,500, so that on a relative frequency basis the low-molecular-weight molecules predominate. The diffusion data shown in Table XVII suggest that a comparable situation exists with the polyurethanes.

10. Future Plans

It is planned to continue the osmometric determinations as described above, using fractionally precipitated polymers in an effort to resolve the diffusion error. If the diffusion error cannot be reduced to an insignificant amount with the higher fractions of the fractionated polymers, an attempt will be made to correct for the diffusion by a rate study of the decrease in osmotic pressure after the maximum has been reached, and extrapolation to zero time. A study of the magnitude of the maximum vs the rate of approach to the maximum for a given fraction will be made, with corresponding measurements of diffusion, preferably on one of the lower fractions. It may also be possible to measure the molecular weight of the diffused polymer by the isopiestic method, by concentrating the solution of diffused polymer by partial evaporation of the acetone. Values of specific viscosity will be obtained for each fraction. The ultimate objective of the studies on the fractionated polymer is to obtain reliable molecular-weight data over a sufficiently wide range of viscosities to calculate the constants in the modified Staudinger equation.**

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*C. F. Bjork, NavOrd Report 1988, NOTS 581, 3 September 1952.

**Aerojet Report No. 540 (19 September 1951), p. 12.

B. SPECIFIC IMPULSES OF NITROPOLYMER-OXIDIZER SYSTEMS

1. Calculations by the Short Method

a. The specific impulses of systems of nitropolymer and ammonium nitrate or ammonium perchlorate are of interest. Using the "short method" reported previously,* values were calculated at several oxidizer compositions up to the stoichiometric for each of the following polymers:

I-A (2,2-dinitro-1,3-propanediol + 3,3-dinitro-1,5-pentane diisocyanate)

I-AN (completely nitrated I-A)

I-J (2-nitro-2-methyl-1,3-propanediol + 3,3-dinitro-1,5-pentane diisocyanate)

I-JN (completely nitrated I-J)

Polydinitrobutyl acrylate

The results are collected in Table XVIII, and represented graphically in Figures 11 and 12. For the pure components, the calculated specific impulses are:

	I_{sp}, lb-sec/lb
I-A	174
I-AN	233
I-J	125
I-JN	202
PDNBA	138
NH_4NO_3	244
NH_4ClO_4	267

b. Differences from the specific impulses reported earlier for these compounds are due to the use of experimental heats of combustion (where available) in place of the predicted values used in the earlier calculations.

*Aerojet Report No. 991/6-2.

TABLE XVIII

SPECIFIC IMPULSES OF NITROPOLYMER-OXIDIZER SYSTEMS

Polymer	Stoichiometric wt% NH_4NO_3	I_{sp}, lb-sec/lb, at Following wt% NH_4NO_3							
		30	40	50	60	65	70	75	Stoich.
I-A, $[C_{10}H_{14}N_6O_{12}]_n$	74.5	--	--	218	224	--	230	--	232
I-AN, $[C_{10}H_{12}N_8O_{16}]_n$	61.5	237	239	240	--	--	--	--	241
I-J, $[C_{11}H_{17}N_7O_{10}]_n$	81.2	--	--	204	--	219	--	228	232
I-JN, $[C_{11}H_{15}N_7O_{14}]_n$	72.6	--	224	228	--	234	--	--	236
PDNBA, $[C_7H_{10}N_2O_6]_n$	82.7	--	--	208	--	221	--	229	234

Polymer	Stoichiometric wt% NH_4ClO_4	I_{sp}, lb-sec/lb, at Following wt% NH_4ClO_4					
		20	30	40	50	60	Stoich.
I-A, $[C_{10}H_{14}N_6O_{12}]_n$	63.2	203	215	226	235	--	247
I-AN, $[C_{10}H_{12}N_8O_{16}]_n$	48.45	244	248	252	--	--	256
I-J, $[C_{11}H_{17}N_7O_{10}]_n$	71.8	173	194	208	222	235	248
I-JN, $[C_{11}H_{15}N_7O_{14}]_n$	60.8	222	231	238	245	--	252
PDNBA, $[C_7H_{10}N_2O_6]_n$	73.7	181	198	213	227	238	252

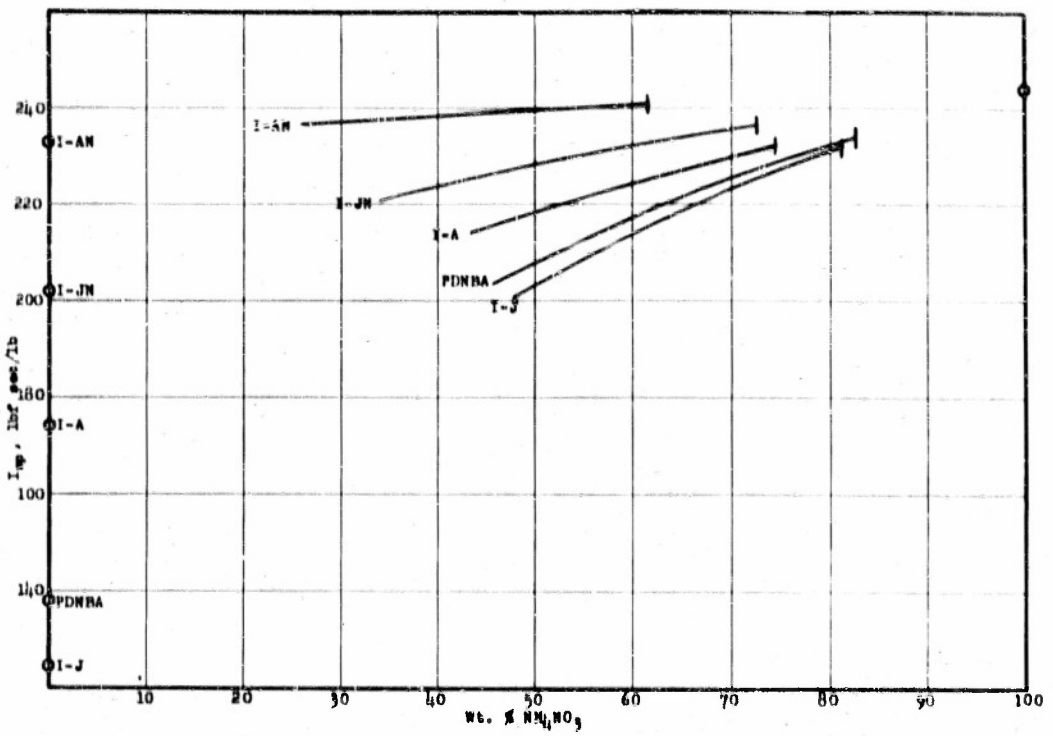

Figure 11

Specific Impulses of Nitropolymer-NH_4NO_3 Mixtures
Calculated for 1000 psia by the Short Method

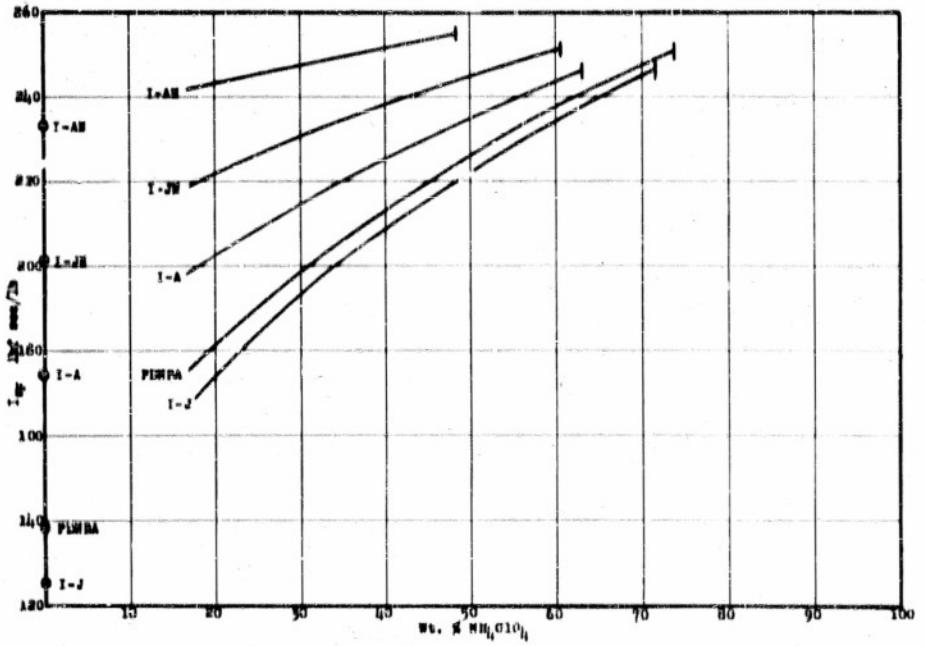

Figure 12

Specific Impulses of Nitropolymer-NH_4ClO_4 Mixtures
Calculated for 1000 psia by the Short Method

2. Accuracy of the Short Method

a. For an indication of the accuracy of the short method as applied to these systems, specific impulses of the system I-JN/NH_4NO_3 were recalculated at length by the exact method, for 1000-psia chamber pressure. The procedure assumes mobile equilibrium in the exhaust gases. The comparison is shown in Table XIX.

TABLE XIX

COMPARISON OF SPECIFIC IMPULSE CALCULATIONS

Composition, wt%		I_{sp}, lb-sec/lb			
I-JN	NH_4NO_3	Short Method	Exact Method	ΔI_{sp}	Temp, T_c, °K
100	0	202.4	202.5	-0.1	1845
80	20	214.3	214.8	-0.5	2094
70	30	219.5	220.1	-0.6	2220
60	40	224.0	224.2	-0.2	2332
50	50	228.4	227.6	+0.8	2440
35	65	234.0	234.7	-0.7	2551
27.44 (stoichiometric)	72.56	236.4	234.9	-1.5	2685

Because of the generally low flame temperatures, dissociation effects were ignored. The agreement obtained was excellent.

b. A similar comparison was made for a group of compositions containing NH_4ClO_4. With this oxidizer, flame temperatures are higher and it is necessary in some cases to take dissociation into account. Further comparisons will be made for such cases. In the meantime, ignoring dissociation, the comparison given in Table XX was obtained; values for which the influence of dissociation may be appreciable are shown in parentheses.

TABLE XX

COMPARISON OF SPECIFIC IMPULSE CALCULATIONS, II

Composition	I_{sp}, lb-sec/lb			
	Short Method	Exact Method (Ignoring Dissociation)	ΔI_{sp}	Chamber Temp, T_c, °K
80% I-A, 20% NH_4ClO_4	202.6	206.4	-3.8	1970
80 I-AN, 20	243.7	(246.3)	--	3240
80 I-JN, 20	222.3	224.7	-2.4	2420
50 I-JN, 50	245.1	(249.3)	--	--

3. Generalized Charts for Specific Impulses of Nitropolymer-Oxidizer Systems

Figures 13 and 14 were constructed on the basis of the data of Table XVIII. They permit the rapid estimation of the specific impulse of a mixture of a nitropolymer and ammonium nitrate or ammonium perchlorate. First, the fuel oxygen balance, O_F, is calculated from the relation

$$O_F = \frac{1600}{M}\left(O - 2C - \frac{H}{2}\right)$$

where C, H, and O are the numbers of gram-atoms of carbon, hydrogen, and oxygen in a gram-formula-weight M of the fuel. Figure 15 or Figure 16 is then used to find the percentage of oxidizer required to oxidize the fuel to carbon dioxide and water. Next, the specific impulse, I_o, of the nitropolymer at 1000 psia is estimated by the short method.* Finally, Figure 13 or Figure 14 is used to estimate the specific impulse of the stoichiometric mixture and other mixtures with oxidizer. In using this procedure it is necessary to calculate the stoichiometric point and to confine the estimates to percentages of ammonium nitrate corresponding to this point or below.

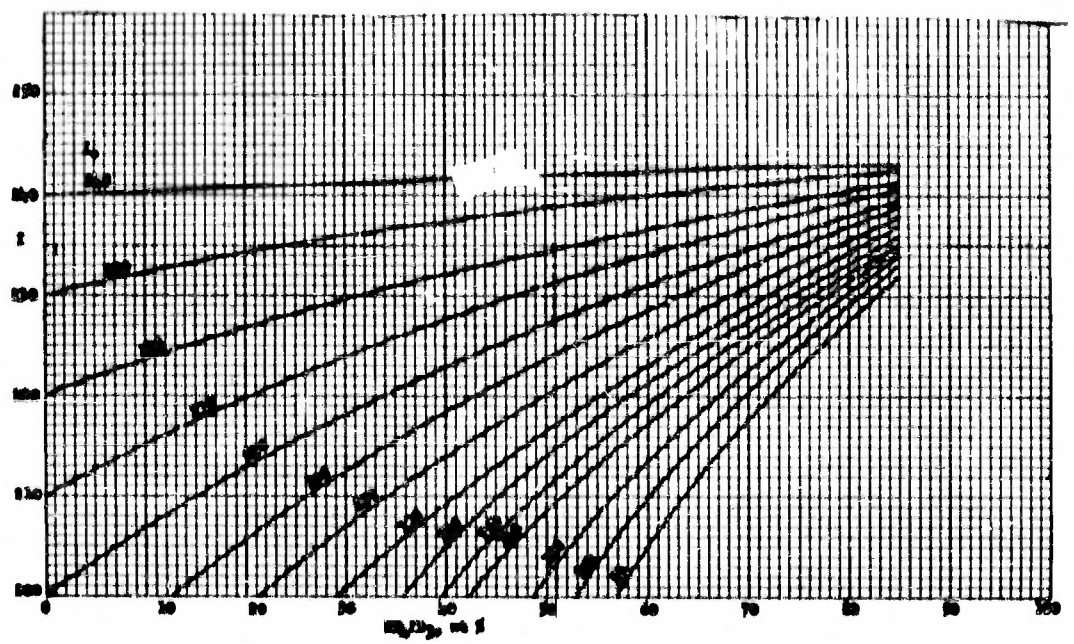

Figure 13

Specific Impulse, I, at 1000 psia for Mixtures of a Nitropolymer of Specific Impulse, I_o, with Ammonium Nitrate

*Aerojet Report No. 991/6-2.

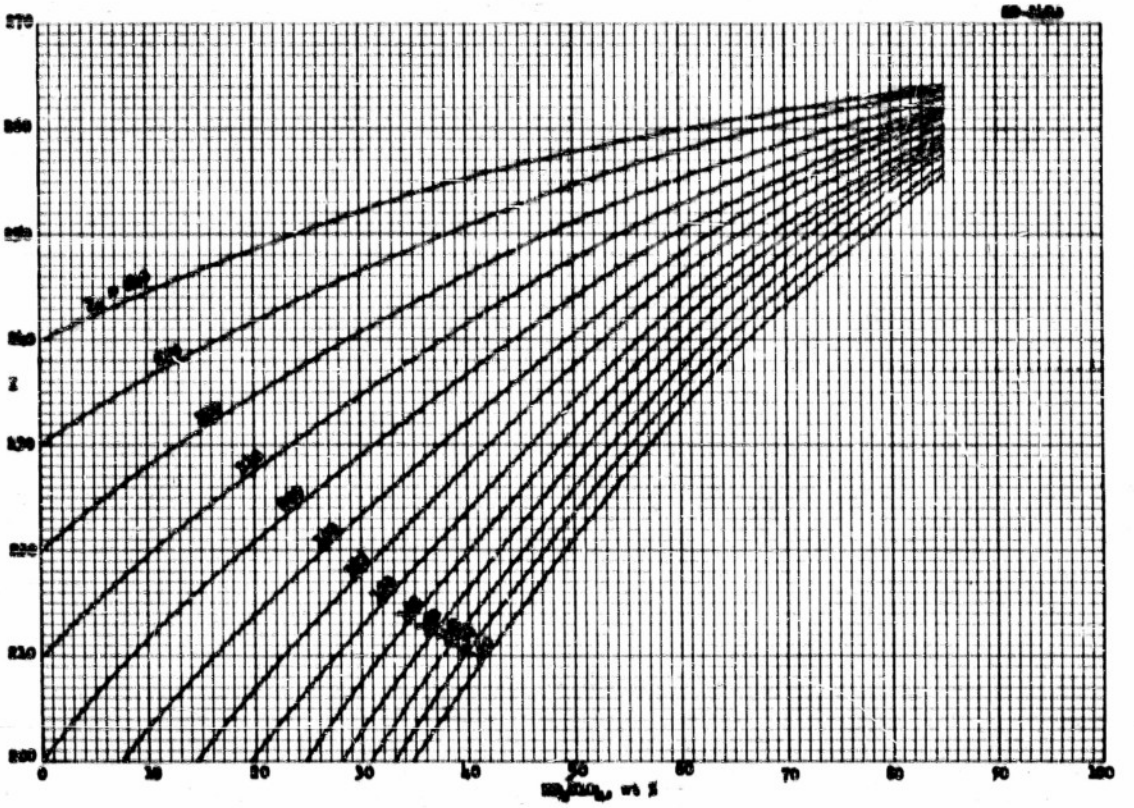

Figure 14

Specific Impulse, I, at 1000 psia for Mixtures of a Nitropolymer of Specific Impulse, I_o, with Ammonium Perchlorate

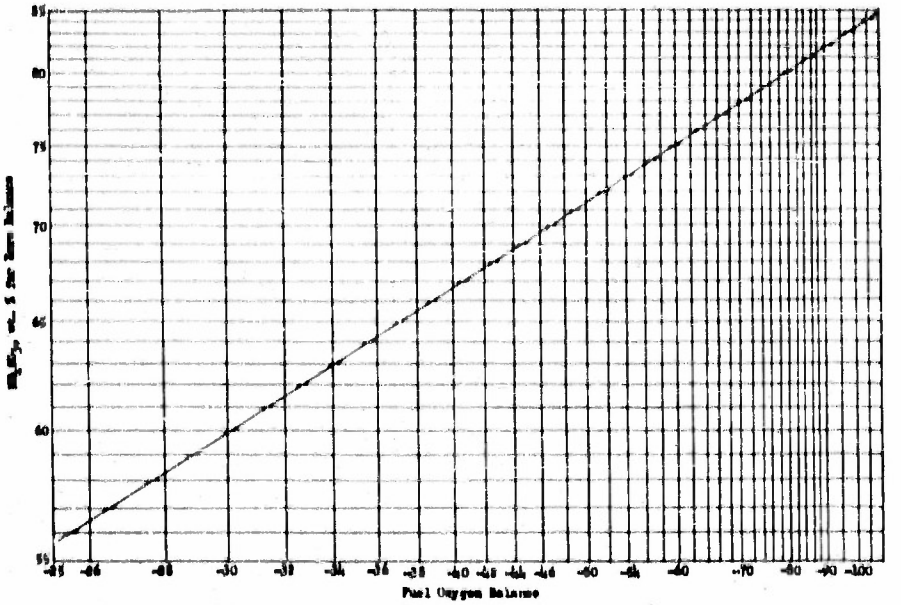

Figure 15

Percentage of Ammonium Nitrate Required to Oxidize a Fuel to Carbon Dioxide and Water

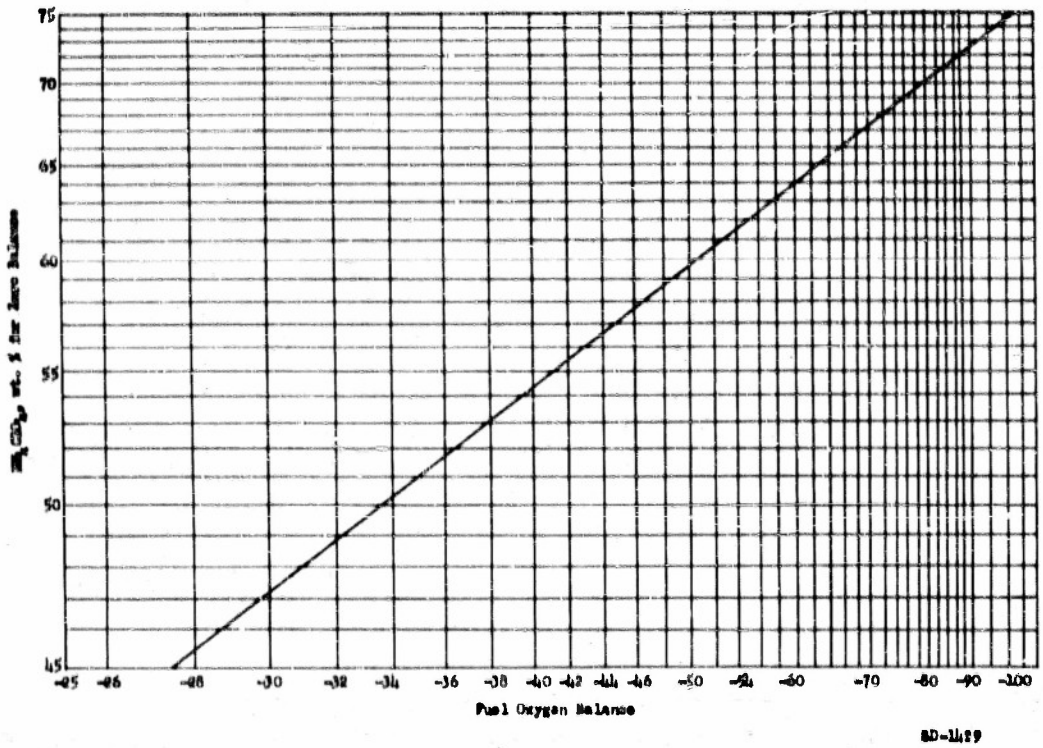

Figure 10

Percentage of Ammonium Perchlorate Required to Oxidize a Fuel to Carbon Dioxide and Water

IV. TECHNICAL PROGRESS: FORMULATION STUDIES

A. FORMULATION OF MIXED POLYMERS

1. Introduction

Amorphous nitropolymers as such do not possess the physical and mechanical properties required for direct use as propellant grains. The objective in these formulation studies is to find a means for preparing propellant grains from the available nitropolymers. One method, as recorded in previous reports, is the polymerization of a vinyl monomer which acts as a dispersing solvent for the amorphous nitropolymers. The present report deals with the continuation of this phase, particularly with respect to obtaining more information on the curing conditions necessary with variation in monomer type and monomer concentration. The effect of inorganic oxidizers formulated with nitropolyurethanes was also investigated, and the study of the stability requirements of nitropolymers has been continued.

2. Polymerization of 2,2-Dinitrobutyl Acrylate in Presence of Polyurethane I-J

a. Discussion

(1) When a mixture of 75% polyurethane I-A (high molecular weight; $\eta_r^{1\%} = 1.51$) and 25% 2,2-dinitrobutyl acrylate was mixed,

only incomplete blending was achieved. Polyurethane I-J is very fluffy, and even an equal weight of 2,2-dinitrobutyl acrylate was quickly absorbed to form an incompatible mixture. Because of this incompatibility, when such mixtures were worked on the roller mill or pressed in the burning-rate-strand die, the 2,2-dinitrobutyl acrylate was largely squeezed out.

(2) The roughly homogeneous product prepared by mixing the components in a beaker cured readily. After partial polymerization of the 2,2-dinitrobutyl acrylate was achieved, the mixture could then be thoroughly blended on the roller mill without any oiling out of the acrylate. A homogeneous, compatible product was obtained, but some degradation of the polymer resulted. The product obtained is tough and flexible and is being cured further. Formulation of 75/25 I-J/DNBA by the above procedure does not yield a physically satisfactory product. Work on intermediate composition formulations is under way.

(3) A mixture of 70% polyurethane I-J (JRF-188), a polymer which is partially cross-linked, 30% 2,2-dinitrobutyl acrylate, and 0.5% MAKP as a catalyst cured well both with and without 1% N-methyl p-nitroaniline at room temperature. The mixture was prepared by blending the components thoroughly on a roller mill. No oiling out of 2,2-dinitrobutyl acrylate was observed. The polyurethane I-J used was a high-molecular-weight polymer (η_r = 2.64, 1% in acetone) and was also incompatible with 2,2-dinitrobutyl acrylate. The product obtained when cured is friable. The samples containing stabilizer cured more completely at both room temperature and 65.5°C, as judged by the increase in viscosity of solutions of the samples. This experiment suggests the use of partly cross-linked polymers in formulation studies.

b. Experimental

The 70/30 formulation samples were prepared by mixing the components on the roller mill, and were cured at room temperature in desiccators containing a nitrogen atmosphere. When cured later at 45°C, the samples were sealed in glass tubes under nitrogen. The results are compiled in Table XXI.

3. Polymerization of 2,2-Dinitrobutyl Acrylate in the Presence of Polyurethane I-A

a. Discussion

When a mixture of 70% polyurethane I-A (composite of JKE-118 and JKE-119) and 30% 2,2-dinitrobutyl acrylate was prepared, complete compatibility was observed. Judging from the relative-viscosity measurements, the mixture did not cure to any greater extent in the presence of any particular catalysts or in the presence or absence of stabilizers. Variations in temperature from room temperature to 65°C had little effect on curing. Other mixtures, such as a 50/50 mixture, cured only partially and slowly, but

somewhat more completely than a 75/25 I-A/DNBA formulation. All these formulations were compatible, forming almost completely homogeneous, viscous fluids of tacky and rubbery consistency at room temperature.

b. Experimental

Polyurethane I-A, 2,2-dinitrobutyl acrylate, and catalyst were mixed, blended on a roller mill, and placed in well-cleaned test tubes, flushed with nitrogen, and stoppered. When it was noted that little increase in viscosity of solutions was occurring at room temperature, the samples were sealed in glass tubes and heated to 45°C. The data are given in Table XXII. In view of the unsatisfactory results presented in Table XXII, formulations containing greater amounts of polymerization catalysts were prepared. These results, which are essentially negative, are given in Table XXIII.

TABLE XXI

CURING OF I-J (JRF-188)/DNBA[a] FORMULATIONS

Composition	Curing Conditions	ΔVisc.[b] for 1% Solutions in Acetone	
70/30 I-J/DNBA + 1/2% MAKP[c]	5 days at R.T.[d]	+0.29	
	5 days at R.T. + 92 hr at 65.5°C[e]	+0.08	(0.37)[g]
70/30 I-J/DNBA + 1% MNA[f]	5 days at R.T.	+0.24	
	5 days at R.T. + 92 hr at 65.5°C[e]	+0.51	(0.75)[g]

[a]DNBA is 2,2-dinitrobutyl acrylate.

[b]ΔVisc. is for each interval, not cumulative.

[c]MAKP is methyl amyl ketone peroxide.

[d]R.T. is room temperature.

[e]65.5°C refers to the temperature, time, and general conditions of the Warburg stability test run.

[f]MNA is N-methyl p-nitroaniline.

[g]The bracketed Δvisc. values represent the total increase.

TABLE XXII

CURING OF 70/30 AND 75/25 POLYURETHANE I-A/DNBA[a] FORMULATIONS USING LOW CATALYST CONCENTRATIONS

Catalyst	Stabilizer	Curing Conditions	$\eta_r^{1\%}$	$\Delta\eta_r^{1\%}$[j]
70/30 Formulations				
None	None; 100% I-A	None	1.51	--
1/4% MAKP[b]	None	96 hr at R.T.[i] + 700 at 45°C	1.36	+0.09
1/4% MAKP	1% MNA[c]	96 hr at R.T. + 700 at 45°C	1.33	+0.09
		96 hr at R.T. + 700 at 45°C + 48 at 65°	1.35	+0.02
1/4% AZO[d]	None	96 hr at R.T. + 192 at 45°C	1.32	+0.05
		96 hr at R.T. + 192 at 45°C + 89 at 65°	1.33	+0.01
1/4% AZO	1% MNA	96 hr at R.T. + 192 at 45°C + 89 at 65°	1.37	+0.11
		96 hr at R.T. + 192 at 45°C	1.35	-0.02
75/25 Formulations				
C-1[e]	1/2% S-1[f]	115 hr at R.T.	1.30	-0.01
		790 hr at R.T.	1.30	0.00
		115 hr at R.T. + 500 hr at 45°C	1.32	+0.01
		115 hr at R.T. + 500 hr + 48 hr at 65°C	1.35	+0.03
		115 hr at R.T. + 500 hr +168 hr at 65°C	1.31	-0.04
C-1	2% of S-1	115 hr at R.T.	1.30	-0.02
		115 hr at R.T. + 70 hr at 45°C	1.34	+0.02
		115 hr at R.T. + 480 hr at 45°C	1.32	0.00
		115 hr at R.T. + 480 hr + 48 hr at 65°C	1.33	+0.01
C-1	1/4 DBU[g]	115 hr at R.T.	1.32	0.00
		115 hr at R.T. + 22 hr at 45°C	1.33	+0.01
		115 hr at R.T. + 430 hr at 45°C	1.34	+0.01
0.25% MAKP	1/2% S-1	115 hr at R.T.	1.30	+0.03
		115 hr at R.T. + 22 hr at 45°C	1.30	0.00
		115 hr at R.T. + 430 hr at 45°C	1.34	+0.04
1/4% MAKP	S-2[h]	115 hr at R.T.	1.28	+0.03
		115 hr at R.T. + 22 hr at 45°C	1.27	-0.01
		115 hr at R.T. + 430 hr at 45°C	1.30	+0.03

[a] DNBA is 2,2-dinitrobutyl acrylate.
[b] MAKP is methyl amyl ketone peroxide.
[c] MNA is N-methyl p-nitroaniline.
[d] AZO is azo-bis-isobutyronitrile.
[e] C-1 is 0.25% benzoyl peroxide plus 0.1% dimethylaniline.
[f] S-1 is equal weights of N-methyl p-nitroaniline plus dibutyl tin dilaurate.
[g] DBU is sym-dibutyl urea.
[h] S-2 is 0.25% dibutyl tin dilaurate plus 1.0% N-methyl p-nitroaniline.
[i] R.T. is room temperature.
[j] $\Delta\eta_r^{1\%}$ is for each interval, not cumulative.

TABLE XXIII

CURING OF I-A/DNBA[a] FORMULATIONS
USING HIGHER CATALYST CONCENTRATIONS

Ratio I-A/DNBA	Catalyst	Stabilizer	Curing	$\eta_r^{1\%}$	ΔVisc.[b]
100% I-A	None	None	None	1.51	--
75/25	C-2[c]	None	20 hr at 45°C	1.24	-0.02
75/25	C-3[d]	1% Sn[e]	20 hr at 45°C	1.26	-0.03
75/25	1/2 C-3	1/2% Sn	20 hr at 45°C	1.27	-0.03
50/50	1/2 C-3	1/2% Sn	20 hr at 45°C	1.23	+0.01
75/25	C-2	None	40 hr at 45°C	1.29	+0.05
75/25	C-3	1% S-1	40 hr at 45°C	1.29	+0.03
75/25	1/2 C-3	1/2% S-1	40 hr at 45°C	1.29	+0.02
50/50	1/2 C-3	1/2% S-1	40 hr at 45°C	1.29	+0.06
75/25	C-2	None	90 hr at 45°C	1.30	+0.01(+0.04)[f]
75/25	C-3	1% S-1	90 hr at 45°C	1.31	+0.02
75/25	1/2 C-3	1/2% S-1	90 hr at 45°C	1.32	+0.03
50/50	1/2 C-3	1/2% S-1	90 hr at 45°C	1.32	+0.03
75/25	C-3	1% S-1	160 hr at 45°C	1.30	-0.01
75/25	1/2 C-3	1/2% S-1	160 hr at 45°C	1.32	+0.00
50/50	1/2 C-3	1/2% S-1	160 hr at 45°C	1.37	+0.05
75/25	C-3	1% S-1	160 hr at 45° + 95 at 65°	1.29	-0.01(0.00)
75/25	1/2 C-3	1/2% S-1	160 hr at 45° + 95 at 65°	1.33	+0.01(+0.03)
50/50	1/2 C-3	1/2% S-1	160 hr at 45° + 95 at 65°	1.39	+0.02
50/50	1/2 C-3	1/2% S-1	160 hr at 45° +150 at 65°	1.42	+0.03(+0.20)

[a]DNBA is 2,2-dinitrobutyl acrylate.

[b]The Δvisc. is for each test interval, not cumulative.

[c]C-2 is 0.5% benzoyl peroxide 0.2% dimethyl aniline and 1.0% N-methyl p-nitroaniline.

[d]C-3 is 0.5% benzoyl peroxide, 0.2% dimethyl aniline, 0.5% azo-bis-isobutyronitrile, 1.0% N-methyl p-nitroaniline and 1.0% dibutyl tin dilaurate.

[e]Sn is dibutyl tin dilaurate.

[f]The bracketed Δvisc. values represent the total change for the formulation.

4. Polymerization of Methyl Methacrylate in Presence of Polyurethane I-A

a. Discussion

(1) In view of the great retardation of the polymerization of 2,2-dinitrobutyl acrylate by polyurethane I-A, it was considered of interest to prepare I-A formulations in which 2,2-dinitrobutyl acrylate was replaced by methyl methacrylate. Methyl methacrylate polymerizes very rapidly to a high-molecular-weight polymer. It was cured in the presence of polyurethane I-A in the ratio of 10 and 25%. The influence of I-A on the polymerization of methyl methacrylate was determined by viscosity measurements. Similar formulations in 2,2-dinitrobutyl acrylate were also prepared for comparison.

(2) While hard, solid products were obtained, the relative viscosity of the 90/10 MMA/I-A formulation was half that of the polymethyl methacrylate. The 75/25 product had a still lower viscosity. Under the same conditions, 2,2-dinitrobutyl acrylate without any I-A added polymerized much more slowly than any of the methyl methacrylate samples.

(3) Ten and 25 percent of polyurethane I-A do not, however, have any marked effect on the polymerization of 2,2-dinitrobutyl acrylate. There is a marked difference between the effect of 10 or 25% I-A as compared with that of 75% or even 50% of I-A.

(4) A gem dinitro group has moderately active chain-transfer properties. It appears the polyurethane I-A, which contains two gem dinitro groups and two active urethane hydrogens per polymer unit, is an effective chain-transfer agent. In minor amounts in 2,2-dinitrobutyl acrylate, the chain-transfer activity of polyurethane I-A is apparently no greater than that of the gem dinitro group in DNBA. In higher concentration, some other factor may become important.

b. Experimental

(1) Two formulations were prepared by dissolving 10 and 25% of polyurethane I-A in a solution of methyl methacrylate containing 0.5% methyl amyl ketone peroxide as a polymerization catalyst. Polyurethane I-A dissolved very readily and quickly. The solutions were placed in sealed tubes in the usual manner and cured at room temperature and then 45°C. From the data, presented in Table XXIV, the decrease in the values of the relative viscosities indicates strong retardation in the polymerization of MMA.

(2) Whereas a 1:1 mixture of I-A and 2,2-dinitrobutyl acrylate seemed to form a complete solution, neither a 10% nor a 25% quantity of polyurethane I-A would dissolve completely in 2,2-dinitrobutyl acrylate. After a week's stirring in test tubes with close clearance between the stirrer and test tube wall, almost complete mixing was obtained. It appeared that some polymerization also occurred. The data are presented in Table XXV.

TABLE XXIV

CURING OF I-A/MMA[a] FORMULATIONS AND MMA AND DNBA[b] BY THEMSELVES[c]

Composition	Curing Conditions	$\eta_r^{1\%}$
MMA	3 days at R.T. + 2 days at 45°C	4.02
90/10 MMA/I-A	3 days at R.T. + 2 days at 45°C	2.03
75/25	3 days at R.T. + 2 days at 45°C	1.71 1.69
DNBA	3 days at R.T. + 2 days at 45°C	1.38 1.38

[a]MMA is methyl methacrylate.

[b]DNBA is 2,2-dinitrobutyl acrylate.

[c]All formulations contain 0.5% methyl amyl ketone peroxide.

TABLE XXV

CURING OF 10/90 AND 25/75 I-A/DNBA[2] FORMULATIONS

Composition	Curing Conditions	$\eta_r^{1\%}$
10/90 I-A/DNBA	None[b]	2.17
10/90 I-A/DNBA	7 days at 45°C	2.23
25/75 I-A/DNBA	None[b]	1.86
25/75 I-A/DNBA	7 days at 45°C	1.98

[a]DNBA is 2,2-dinitrobutyl acrylate.

[b]Qualified by an unknown amount of polymerization of the DNBA which may have occurred during the week of stirring.

5. Polynitrourethane-Ammonium Nitrate and Polynitrourethane-Ammonium Perchlorate Formulations

a. Formulations with Polynitrourethane I-A

(1) Discussion

(a) Specific-impulse calculations for mixtures of various nitropolymers with inorganic oxidizers such as ammonium nitrate or

ammonium perchlorate show that the performance of a relatively low-energy nitropolymer can be greatly improved by incorporation of a small amount of inorganic oxidizer (see p. 35). The objectives of the preliminary studies reported at this time are to determine the effect of the ammonium nitrate and ammonium perchlorate addition on the burning rate, to note the gross physical characteristics of the strands produced, and to determine in a preliminary way the necessary procedures for preparing the strands and other test specimens.

(b) Using polyurethanes I-A and I-J, 50:50% mixtures have been prepared in a ball mill with both ammonium nitrate and ammonium perchlorate. The material obtained is reasonably uniform. All blends were found more sensitive to impact and to thermal decomposition than the starting polyurethanes (Table XXVI).

TABLE XXVI

PHYSICAL PROPERTIES OF I-A AND I-J/NH_4ClO_4, 50/50 FORMULATIONS

Composition	Impact Sensitivity 2-kg wt, cm	Max Temp Without Flaming °C	Flare-up Temperature, °C	
			20 sec	1 sec
I-A/NH_4ClO_4 50/50	7-8	240	250	270
I-J/NH_4ClO_4 50/50	12-13	252-253	260	300

(c) The burning rate strands of polyurethane I-A–ammonium nitrate were obtained by pressing 4 g or 8 g of the mixture at 150°F and 7000 lb/sq inch.* Crystallization of the ammonium nitrate appears to occur shortly after the fused samples are released from the die. The results for 50/50 I-A–ammonium nitrate at 1000 lb pressure and 60°F indicate no material change in the burning rate of 0.12 in./sec previously obtained for low-molecular-weight I-A. The burning rate for strands about 3 mm thick (using 4 g of material) is the same as for samples about twice as thick (8 g of material). The uniform rate for the first and second inch may be interpreted to indicate good uniformity of blending.

(2) Experimental

(a) A composite I-A prepared from JKE-118 and JKE-119 was used. The ammonium nitrate was 30% fine and 70% coarse grade, as used in Aeroplex formulations. The 50-50 mixture was first tumbled in a jar

*Aerojet Report No. 638, p. 67.

on a roller for 24 hours. A sample pressed in the burning rate stand die showed obvious nonhomogeneity. The mixture was then ball-milled in the same jar on a roller for 20 hours.

(b) The desired size of I-A/NH_4NO_3 sample was weighed into the die and pressed at 120°F and 7000 lb/sq in. on a Carver press. After 15 minutes, the temperature was increased to 150°F for 15 minutes. The temperature was then gradually dropped to 60°F over a half-hour period, keeping the pressure at 7000 lb/sq in. The samples were fused evenly at 120°F, and no obvious additional change occurred at 150°F. When removed from the die, the samples were fairly homogeneous in appearance and had a fused, gray-brown appearance. On standing in a stoppered tube, the samples became more grayish in color and "crystallized" in appearance. The I-J/NH_4NO_3 and the ammonium perchlorate formulations will be burned in the near future. The ball-milled mixture detonated at a 25- to 30-cm drop of a two-kilogram weight. Samples did not explode or ignite when dropped into a Wood's metal bath at 270°C. After a few seconds they gradually fumed off. The pressed samples fumed off at 270 to 300°C (Tables XXVI and XXVII).

TABLE XXVII

PHYSICAL PROPERTIES OF I-A AND I-J/NH_4NO_3 50/50 FORMULATIONS

Composition	Impact Stability 2-kg wt, cm	Fume-off Temperatures °C	
		20 sec	1 sec
50/50 I-A/NH_4NO_3	25 to 30	265	275
50/50 I-J/NH_4NO_3	60 to 75	300 (1 min)	--

(c) The Crawford bomb burning-rate results are given in Table XXVIII. These samples were restricted by the usual coating procedure with several coats of Krylon.

TABLE XXVIII

CRAWFORD-BOMB BURNING-RATE TESTS AT 1000 LB AND 60°F

Milling Batch	Wt Sample, g	1-in. Time, sec	2-in. Time, sec
1	4	8.280	16.430
1	8	8.041	16.013
2	4	8.331	9.915[a]
2	8	8.110	16.090

[a] The lead wires were fused close on one side, indicating a flash down the side.

6. Manometric Studies

a. Discussion

(1) Severe stability requirements have been found to be an important factor in the formulation of nitropolymers.* Only the nitropolymers which pass the potassium iodide starch-paper test at 65.5°C and produce a minimum evolution of gas in the Warburg-manometer test (Figure 17) are suitable for formulation work. In order to find a correlation between these two tests a series of nitropolymers and their mixtures have been investigated. The results of this investigation are compiled in Table XXIX.

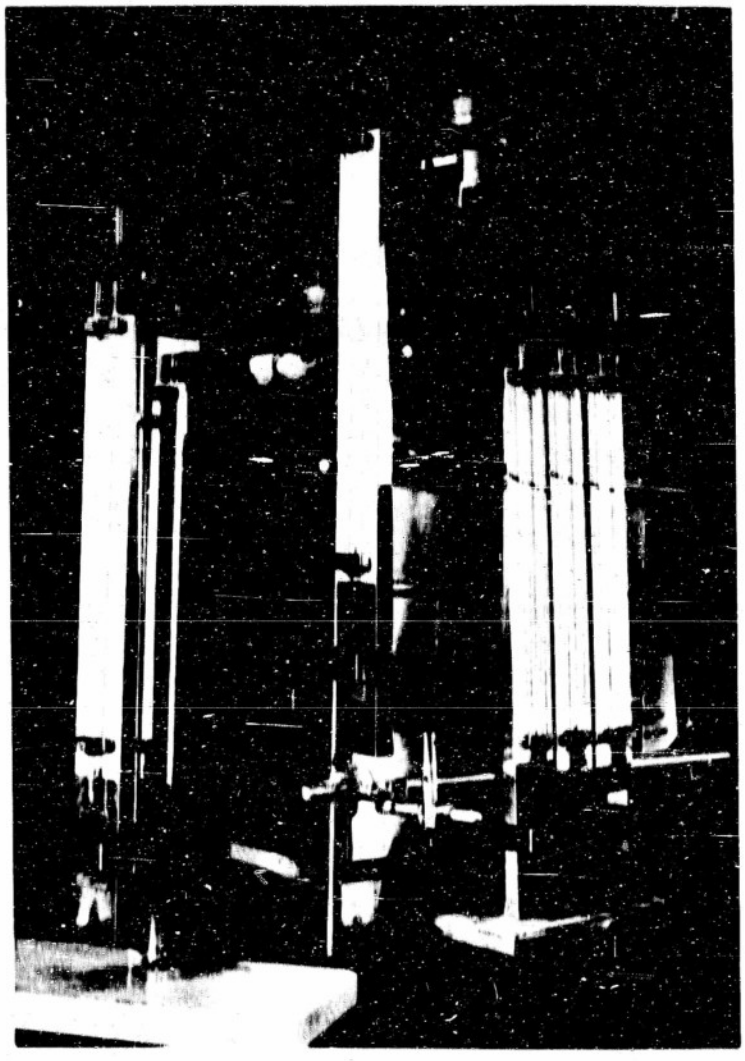

Figure 17
Warburg Apparatus

*Aerojet Report No. 663, p. 60.

TABLE XXIX

WARBURG STABILITY TESTS ON POLYURETHANES AND THEIR FORMULATIONS WITH DNBA[a]

Material	Curing	Gas Evolution, ml per 100 g per hour[b]	65.5°C KI-Starch Paper Stability Test Time
I-A, JKE 111	None	-0.03 for 61 hr[c]	35 min
I-H, JKE 96	None	+0.11 for 87 hr[c]	15 min
I-H, JKE 55	None	+0.01 for 165 hr[c]	—
I-H, JKE 120	None	+0.14 for 216 hr[c]	—
I-O, JKE 76	None	-0.04 for 188 hr[c]	—
I-A, JKE 115	None	+0.11 for 140 hr	4 + hr
70/30 Above I-A/DNBA[d]	4 days at R.T.[e]	+0.05 for 87 hr	2-1/2 hr
As above + 1% MNA[f]	4 days at R.T.	+0.06 for 87 hr	3 hr
70/30 Above I-A/DNBA[g]	4 days at R.T.	+0.08[i] for 87 hr	4 + hr
As above + 1% MNA	4 days at R.T.	+0.09[i] for 87 hr	4 + hr
75/25 Above I-A/DNBA[j]	24 hr at R.T.	+0.15 for 87 hr	—
I-A, Composite of JKE 118 and 119	None	+0.04 for 142 hr	k
I-J, JRF-188	None	-0.36 for 75 hr[c]	25 min[k]
70/30 Above I-J/DNBA[l]	5 days at R.T.	-0.04 for 92 hr[c]	35 min[k]
As above + 1% MNA	5 days at R.T.	-0.03 for 92 hr[c]	35 min[k]
I-J, JRF 181	None	+0.05 for 40 hr	k
I-J, JRF 188	None	+0.10 for 39 hr[m]	k
I-J, JRF 189	None	+0.02 for 69 hr	k
I-J, JRF 192 Composite	None	+0.03 for 69 hr	k
I-J, Composite of above 4	None	-0.02 for 121 hr	

[a] DNBA is 2,2-dinitrobutyl acrylate.

[b] These figures are 100 times the bracketed values given in Tables XXXII and XXXIII of Aerojet Report No. 663, pp. 62 and 63. Are vol/wt% per hour.

[c] These values are for polyurethanes as received and not specially dried at 40°C and high vacuum. These polyurethanes are stable (under 0.10 ml gas per 100 g per hour) but have traces of volatiles.

[d] 1/4% Of methyl amyl ketone peroxide based on weight of DNBA present.

[e] R.T. is room temperature.

[f] MNA is N-methyl-p-nitroaniline.

[g] 1/4% Of azo-bis-isobutyronitrile is present in DNBA.

[i] These values are corrected for gas (N_2) evolution due to decomposition of azo catalyst.

[j] A mixed catalyst-stabilizer consisting of 1/4% benzoyl peroxide, 0.1% dimethyl aniline, 1/4% N-methyl-p-nitroaniline and 1/4% dibutyl tin dilaurate present in DNBA.

[k] These polyurethanes and formulations showed very slight discoloration of the paper after about 20 minutes or the times indicated. No marked coloration occurred even after several hours.

[l] 1/2% Of methyl amyl ketone peroxide is present in the DNBA.

[m] This sample of I-J (JRF-188) was thoroughly dried, as are all materials which are not accompanied by footnotes.

(2) Although nitropolyurethanes seemed to be stable in both tests the postnitrated polyurethanes to date have been found to be somewhat inferior. Table XXX is a compilation of stability results obtained by the study of various postnitrated polymers.

TABLE XXX

WARBURG STABILITY TESTS ON POSTNITRATED POLYURETHANES

Material	Gas Evolution, ml per 100 g per hr[a]	65.5°C KI-Starch Paper Stability Test Time
I-JN, JRF-193	1.73 for 45 hr	20 min
I-JN, JRF-194	1.66 for 44 hr	2 hr
I-JN, JRF-193[b]	0.91 for 45 hr	—
I-JN, JRF-193[c]	0.64 for 45 hr	—
I-JN, JRF-194[d]	0.94 for 45 hr	—
I-JN, JRF-193-A	0.96 for 45 hr	45 min
I-JN, JRF-193-B	1.15 for 45 hr	80 min
I-JN, JRF-193-C	1.48 for 45 hr	4 + hr
I-JN, JRF-193-C	1.41 for 45 hr	4 + hr
I-JN, JRF-208-B	1.38 for 45 hr	--
I-AN, JKE-117-B	—	2 min
I-HN, JKE-116	1.68 for 45 hr	—

[a]These values are the same as in Table X and are 100 times the bracketed values given in Tables XXXII and XXXIII of Aerojet Report No. 663, pp. 62 and 63.

[b]Dried for 8 hr at room temperature and 1μ pressure.

[c]Dried for 8 hr at 40°C and 1μ pressure.

[d]Dried for 8 hr at room temperature and 8 hr at 40°C and 1μ pressure.

(3) Mixtures of polyurethanes I-A and I-J with ammonium nitrate have been investigated in both the 65.5°C test and Warburg-manometer test. It has been found that addition of inorganic oxidizers, although it increased the oxygen balance, did not change the thermal stability of the mixtures (Table XXXI).

TABLE XXXI

WARBURG STABILITY TESTS OF I-A AND I-J AMMONIUM NITRATE FORMULATIONS[a]

Material	Gas Evolution, ml per 100 g per hour	65.5°C KI-Starch Paper Stability Test Time
I-A/NH_4NO_3 50/50	+0.1 during first 24 hr -0.03 for 10-day run	4 + hr
I-J/NH_4NO_3 50/50	+0.2 during first 3 hr -0.06 for 12-day run	4 + hr

[a]Neither formulation was dried under high vacuum. Both show traces of volatiles.

(4) In some cases negative values were observed where one might expect increased gas evolution. This is explained by the experimental procedure used. When the Warburg reaction flask is placed in the 65.5°C bath, the manometer venting stopcock is left open for a half hour to permit the vessel and contents to come up to bath temperature. A volatile component will have time to vaporize to its vapor pressure for 65.5°C but will not have time to distill into the colder parts of the assembly. A certain amount of nitrogen will be displaced before the manometer stopcock is closed. In time, however, this volatile component will distill into the colder parts of the assembly. The vapor pressure of this material will then drop to that corresponding to the temperature of the colder part of the equipment and an apparent "absorption" will be evident in the manometer reading. This explanation is supported by the fact that in one experiment the condensate was identified by means of a mass spectrographic analysis as dioxan. This would be a likely contaminant because it is used as a solvent in the polyurethane preparation.

(5) On the other hand, when temperature stability was reached an initial rapid gassing was observed, which later was completely "absorbed." This observation is explained in the same manner. When the volatile component is less volatile or present to a smaller extent, the half-hour warmup period may not be long enough for it to reach its ultimate vapor pressure. After equilibrium is reached, it may not be volatile enough or present in great enough amount to condense into the cooler parts of equipment to produce an apparent "absorption" (see Figure 18).

(6) A study was carried out to attempt the identification of the gaseous products developed from a sample of polyurethane I-JN. Mass spectrographic analyses (Table XV) of the gaseous decomposition products demonstrated the presence of nitrogen and nitric oxide in significant amounts in addition to carbon dioxide. From the intensity it was estimated that for

each molecule of carbon dioxide formed, a half molecule of nitrogen and a quarter molecule of nitric oxide was evolved. When dry polyurethanes I-J and I-H which passed the KI test were tested in the Warburg-manometer assembly using air instead of nitrogen as the confining gas, an absorption of gas occurred. Analysis of the residual gas from the I-J run showed that the oxygen had been completely removed. There was a small amount of carbon dioxide formed, less than one molecule for 20 molecules of oxygen adsorbed. No nitric oxide or water were found in the decomposition gases (Table XVI).

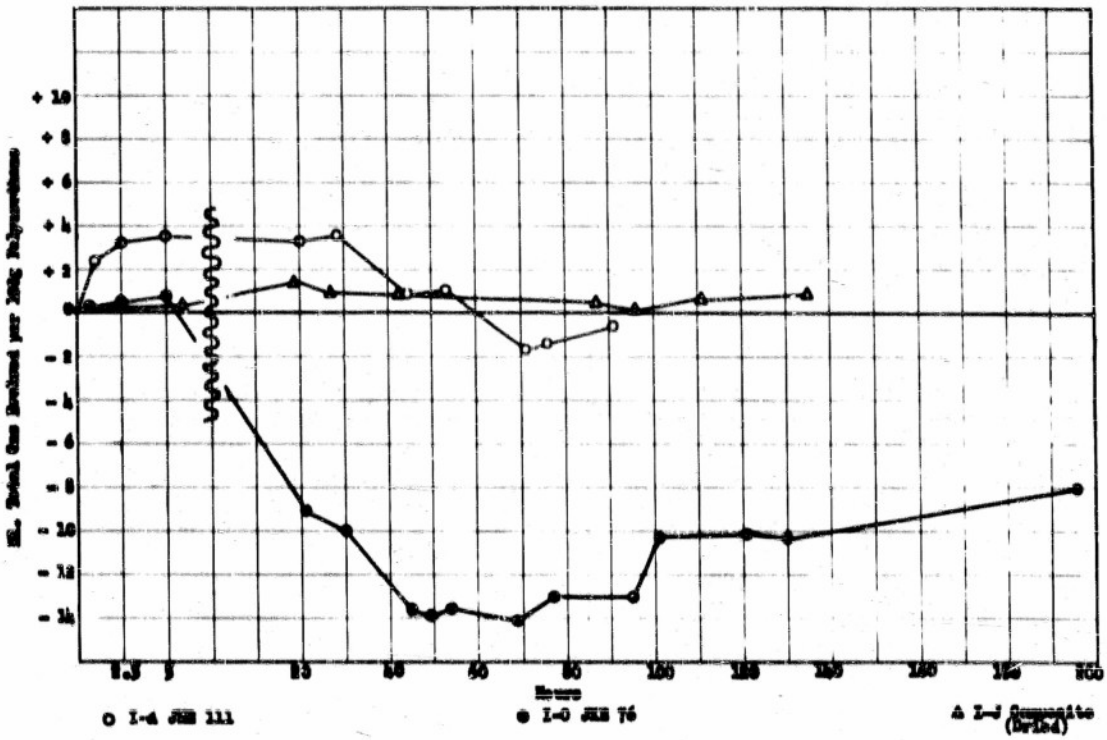

Figure 18

Gas Evolution vs Time in Warburg-Manometer Test

(7) Experience has shown that both the manometric and the starch-iodide tests are required in order to establish the thermal stability of a nitropolymer. However, no correlation has been established between the rate of gas evolution and the oxidizing properties of the decomposition products. In the future all nitropolymers which are to be considered for formulation studies must pass the minimum standards established under both of these tests. These tests will be extremely stringent with respect to the postnitrated polymers, and a satisfactory means must be found to provide them with adequate thermal stability.

b. Experimental

(1) The general procedure for Warburg-manometer determinations has been described earlier.*

(2) When helium was used as the confining gas, the system was evacuated and filled with helium four times. Helium was then flowed through the system for five minutes to drive out small amounts of nitrogen that might enter during each flushing operation. The vessel was heated to temperature while keeping the stopcock closed at the top of the manometer. Only when a positive pressure developed was the stopcock opened momentarily.

(3) Figure 17, presented on Page 49, shows the present Warburg-manometer assembly for the testing of nitropolymers.

V. TECHNICAL PROGRESS: ORGANIC SYNTHESIS

A. NITRO OLEFINS

1. Introduction

The radical-induced polymerization of vinyl monomers containing nitro groups provides a means for preparing nitropolymers. High-energy monomers containing an adequate number of nitro groups are therefore of interest. Although previous chain-transfer studies have eliminated from consideration the structures containing the trinitromethyl group, work on less active chain-transfer types has been continued. This report deals with the synthesis of 3,3-dinitrobutyl acrylate, attempts to prepare N-2,2-dinitropropyl acrylamide, and with hydroxyethyl acrylamide.

2. Preparation of 3,3-Dinitrobutyl Acrylate

a. Discussion

The synthesis of structural isomeric monomers and their polymerization will help to obtain information on mechanical properties and structure. The synthesis of 2,2-dinitrobutyl acrylate has been reported earlier.** This report deals with the preparation of 3,3-dinitrobutyl acrylate. The new compound was prepared by esterification of 3,3-dinitrobutanol with acrylic acid, using the technique of azeotropic removal of water.***

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*Aerojet Report No. 663 (23 December 1952), p. 61.

**Aerojet Report No. 590, pp. 52-55.

***Aerojet Report No. 663, p. 82.

b. Experimental

A three-necked flask provided with a Dean Stark water separator, thermometer, and stirrer was charged with 82 g 3,3-dinitrobutanol, 93.6 g glacial acrylic acid and 300 ml benzene. One milliliter conc. sulfuric acid was added and the mixture was refluxed. Within ten hours 10 ml of water was evolved. After cooling, the solution was washed with water, 5% sodium hydroxide, and water again. The benzene solution was dried over sodium sulfate, filtered, and concentrated. The remaining viscous oil (102 g) was distilled at 84 to 92°C at 4 microns, and twice redistilled at 78 to 80°C at 2 microns to yield 82 g of faintly yellow 3,3-dinitrobutyl acrylate, n_D^{25} 1.4660.

Anal. Calc'd for $C_7H_{10}N_2O_6$: %C, 38.77; %H, 4.68; %N, 12.86

Found: %C, 38.00; %H, 4.77; %N, 12.62

3. Attempted Preparation of N-(2,2-Dinitro-1-propyl) Acrylamide

a. Discussion

(1) Numerous attempts to prepare N-(2,2-dinitro-1-propyl) acrylamide have thus far failed. Since alkylations of amides with 2,2-dinitro-1-propanol or condensations of hydroxymethyl amides with 1,1-dinitroethane do not proceed, recent efforts have been directed toward the preparation of 2,2-dinitro-1-propylamine.* Using the classical methods of organic chemistry, several obvious synthetic routes are available. The Gabriel synthesis using 2,2-dinitro-1-p-toluenesulfonate and potassium phthalimide has already been shown to be unsuccessful. Another route is via the previously unknown 3,3-dinitrobutyric acid. This acid, by conventional means, through the acid chloride, azide, and isocyanate might be degraded to the desired amine:

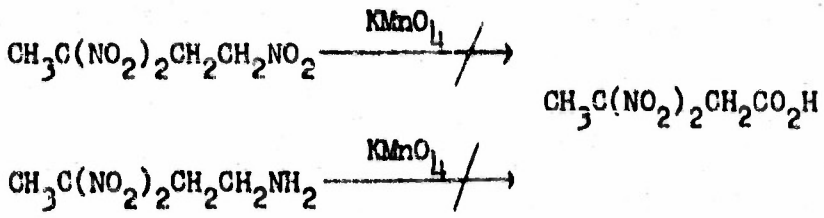
$$CH_3C(NO_2)_2CH_2CO_2H \longrightarrow CH_3C(NO_2)_2CH_2COCl \longrightarrow$$

$$CH_3C(NO_2)_2CH_2CON_3 \longrightarrow CH_3C(NO_2)_2CH_2NCO \longrightarrow$$

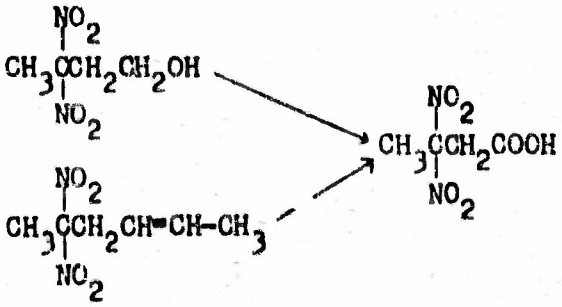
$$CH_3(NO_2)_2CH_2NH_2 \cdot HX$$

(2) Attempts to prepare 3,3-dinitrobutyric acid by oxidation of 1,3,3-trinitrobutane or 3,3-dinitro-1-butylamine in aqueous sulfuric acid with potassium permanganate were not successful.

*Ibid., p. 66.



Only starting materials were recovered. Neutral or alkaline oxidation conditions cannot be used in view of the results of Shechter's studies on the oxidation of dinitrocyclohexane.* However, oxidation of 3,3-dinitro-1-butanol** with permanganate in aqueous sulfuric acid yielded a new acid, mp 88 to 89°C, which is undoubtedly the expected 3,3-dinitrobutyric acid. The same acid was obtained from the oxidation of 5,5-dinitro-2-hexene, as shown in the second equation:



The neutral equivalent and analysis are in agreement with the structure and a mixed melting point without depression confirmed the identity of the product in both preparations.

(3) On treatment with thionyl chloride followed by reduced-pressure distillation, the above-mentioned isolated acid yielded a somewhat unstable yellow oil, n_D^{25} = 1.4731, which is probably the expected acid chloride, although the elemental analysis was poor. The once-distilled acid chloride was treated with sodium azide in acetic acid and the resulting mixture was extracted with chloroform. Decomposition of the azide in the chloroform took place, as evidenced by the evolution of nitrogen. The chloroform solution was heated with aqueous hydrochloric acid and evaporated to dryness. A small amount of crystalline material was isolated which proved to be mainly ammonium chloride and not the expected dinitropropylamine hydrochloride. This reaction will be repeated with larger quantities of dinitrobutyric acid, and intermediates such as the isocyanate will be isolated.

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*Ohio State Report No. 6 (October 1951), p. 10.

**Aerojet Report No. 663, p. 82.

b. Experimental

(1) Preparation of 3,3-Dinitrobutyric Acid

(a) Oxidation of 5,5-Dinitro-2-hexene

A 500-ml three-necked flask fitted with mechanical stirrer and thermometer was charged with 200 ml of 25 wt% sulfuric acid and 8.6 g (0.5 mole) 5,5-dinitro-2-hexene. At -10 to +1°C (ice-salt bath) sodium permanganate trihydrate was added in 4.0-g portions. The reaction was exothermic. The next portion of permanganate was not added until the previous one had been consumed. In the beginning each portion of permanganate required about 10 minutes. After 32 g (theory required 26 g) of permanganate was added, the purple color persisted for at least 45 minutes. At 0 to 5°C, sodium bisulfite was added in small portions until all the manganese dioxide dissolved. The mixture was filtered and the precipitate was washed well with ether. The combined filtrates were charged into a liquid-liquid extractor and the aqueous phase was continuously extracted with ether for 65 hours. The ether layer was separated, dried over Drierite, filtered, and evaporated to dryness. The residue, 7.5 g oily crystals, was taken up in 15 ml anhydrous chloroform. On cooling, colorless plates formed. This was isolated by filtration and washed with cold chloroform to yield 3.1 g colorless plates, mp 86 to 88°C. A second crop of 1.5 g (52% total yield) was obtained by concentration and cooling of the filtrate. A small sample recrystallized from chloroform melted at 88 to 89°C. Further recrystallizations did not raise the melting point and examination of all filtrates failed to yield any other crystalline material. A sample, mp 88 to 89°C, was submitted for elemental analysis.

Anal. Calc'd for $C_4H_6N_2O_6$: %C, 26.97; %H, 3.40; %N, 15.73

Found: %C, 27.24; %H, 3.50; %N, 15.92

(b) Oxidation of 3,3-Dinitro-1-butanol

A one liter three-necked flask fitted with mechanical stirrer and thermometer was charged with 6.0 g (0.0367 mole) crude 3,3-dinitro-1-butanol and 350 ml of 25% by weight sulfuric acid. At about 5 to 8°C, potassium permanganate was added in 2.0-g portions. The next portion was not added until the previous one had been consumed. When the last 2-g portion (10 g total added) gave a purple color which persisted for more than one hour, the excess permanganate and the precipitated manganese dioxide were destroyed by the portionwise addition of sodium bisulfite. The colorless mixture was extracted three times with ether. The ether solution was washed with saturated sodium chloride solution, dried over Drierite, and evaporated to dryness, leaving an oily crystalline residue of 4.2 g. Continuous liquid-liquid extraction of the aqueous phase with ether for four days yielded only 0.3 g more oil. The crude material was recrystallized from chloroform and yielded 3.5 g (54% of theoretical), mp 88 to 89°C, in the form of colorless

plates. A mixed melting point with the acid from 5,5-dinitro-2-hexene (mp 86 to 88°C) as obtained under (1), was 86 to 88°C.

Anal. Calc'd for $C_4H_6N_2O_6$: %C, 26.97; %H, 3.40; %N, 15.73

Found: %C, 31.35; %H, 3.64; %N, 15.09

The disagreement in the carbon value is noteworthy. However, a neutral equivalent determined on the same material from which the sample for elemental analysis had been withdrawn gave the values 183, 182, as compared with the calculated value of 178.

(2) Preparation of 3,3-Dinitrobutyryl Chloride

A 50-ml round-bottom flask was charged with 3.0 g (0.0168 mole) 3,3-dinitrobutyric acid and 6.0 ml thionyl chloride. After standing overnight at room temperature, the crystalline acid had not dissolved. On warming, the crystals dissolved instantly to form a light-green solution which on refluxing soon turned brown. After refluxing for one hour, the evolution of sulfur dioxide and hydrogen chloride practically ceased. The solution was refluxed one half hour longer. The excess thionyl chloride was removed at reduced pressure and the brown oil, 3.1 g, was distilled in a bulb tube in an air bath at 60 to 80°C and 1 to 2 mm pressure to yield 0.2 g yellow forerun, 1.4 g middle cut, and 1.3 g dark-brown, non-distillable residue. The middle cut was redistilled as before to yield 0.4 g forerun and 0.8 g yellow middle cut, n_D^{25} 1.4731, a portion of which was submitted for elemental analysis.

Anal. Calc'd for $C_4H_5N_2O_5Cl$: %C, 24.44; %H, 2.56; %N, 14.26; %Cl, 18.04

Found: %C, 24.82; %H, 3.80; %N, 12.81; %Cl, 19.16

(3) Attempted Degradation via Azide and Isocyanate

(a) A 200-ml three-necked flask fitted with stirrer, thermometer, and ice bath, was charged with 5.2 g once-distilled 3,3-dinitrobutyryl chloride, n_D^{25} 1.4730, and 25 ml glacial acetic acid. A slurry of 5 g (approx. threefold excess) sodium azide in 30 ml acetic acid was added rapidly. The temperature rose to 21°C. The mixture was stirred for 2 hr at 15 to 20°C. After dilution with 80 ml water, the mixture was extracted three times with chloroform. The combined chloroform extract, about 100 ml, was washed twice with water, dried over Drierite a half hour, and filtered. About a third of the volume was distilled to complete the drying. The residue was refluxed 9.5 hr. Nitrogen gas was evolved rapidly in the beginning.

(b) The brown solution was divided into two equal parts. One was evaporated to dryness, yielding 1.0 g brown viscous oil which could not be crystallized. The other was refluxed 3.5 hr with 20 ml conc. hydrochloric acid. The layers were separated. The chloroform layer was

washed with dilute hydrochloric acid and the combined acid solutions were evaporated to dryness. This left a small amount of oily, semi-crystalline material. The mass was taken up with 2 ml ethanol and precipitated with 2 ml acetone and 1 ml ethyl acetate to yield about 40 mg gray crystals, mp 240 to 250°C dec. A sample was sublimed at 1 mm from an oil bath at 150 to 170°C to yield colorless crystals.

Anal. Calc'd for $C_3H_8N_2O_4Cl$: %C, 19.3; %H, 4.3; %N, 22.5

Found: %C, 1.25; %H, 7.32; %N, 24.38

Calc'd for NH_4Cl: %C, 0.0; %H, 7.5; %N, 26.2

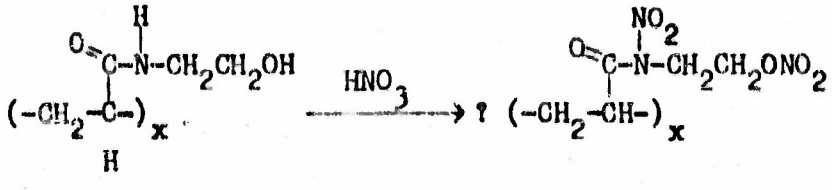
4. Attempted Preparation of Poly-N-nitro-N-(nitratoethyl)-acrylamide

a. Discussion

Attempts to prepare poly-N-nitro-N-(nitratomethyl)-acrylamide (calculated I_{sp} = 229 lbf-sec/lbm) have not been successful to date.* Several small-scale attempts to polymerize hydroxymethyl acrylamide have yielded only insoluble cross-linked polymers. This might be expected from the structure of the monomer, and is in agreement with similar results recently reported by Purdue University. This difficulty may possibly be avoided by going to the next higher homologue, hydroxyethyl acrylamide, which is much less likely to cross-link during polymerization. A recent American patent, U.S.P. 2,593,888, April 22, 1952, reported the preparation of this monomer from acrylyl chloride and monomethanol amine in acetonitrile:

$$CH_2{=}CHCOCl + 2NH_2CH_2CH_2OH \xrightarrow{CH_3CN} CH_2{=}CHCONHCH_2CH_2OH + HOCH_2CH_2NH_3Cl$$

The postnitrated polymer, poly-N-nitro-N(2-nitratoethyl)-acrylamide, has a calculated specific impulse of 209 lbf-sec/lbm. Two attempts to duplicate the patent example for the preparation of hydroxyethyl acrylamide have resulted only in the isolation of polymer. This polymer,



*Aerojet Report No. 663, p. 69.

probably polyhydroxyethyl acrylamide, was isolated and purified. It was nitrated in 100% nitric acid. The resultant polymer gave a heat of combustion corresponding to the introduction of only slightly more than one nitro group per polymer unit instead of the desired two. Further nitration attempts will be made.

b. Experimental

(1) A solution of 45 g (0.5 mole) acrylyl chloride in 40 ml acetonitrile was added with good stirring at 5 to 10°C over about 2 hr to a solution of 61 g (1.0 mole) redistilled ethanolamine in 80 g acetonitrile containing 0.3 g hydroquinone and a trace of trinitrobenzene. The mixture was left overnight at 5°C. The mixture was filtered and the solid was washed with acetonitrile. After addition of 1.2 g more hydroquinone, the combined filtrates, constituting a two-phase system, were evaporated at 1.2 mm on a warm water bath. The residue, a very viscous oil, suddenly began to get very hot. It was cooled with dry ice. The resultant material was a tacky glass at room temperature. The glass was dissolved with methanol and precipitated with acetone three times, using a Waring Blendor, and was then dried in vacuo. The yield of polymer was 19 g of a tan-colored, hygroscopic solid, soluble in water.

(2) A 100-ml three-necked flask fitted with thermometer and stirrer was charged with 30 ml tech. 100% nitric acid. At 0 to 5°C, 4.0 g polyhydroxyethyl acrylamide was added portionwise over about 20 minutes. The material dissolved slowly to give a yellow, viscous solution. After a total of 45 minutes, the solution was poured onto ice. The gummy solid was dissolved with acetone, precipitated with water, and dried. It was then dissolved with acetone and precipitated with water twice more, and thoroughly dried in vacuo. The yield was 3.5 g yellow powder, I.S. = 50 cm/2 kg, softening point 95°C dec. Heat of combustion: Calc'd, 3141 cal/g; found, 3940 cal/g. Calc'd for one nitro group per unit: 4190 cal/g.

B. NITRO ALCOHOLS

1. Introduction

Nitro diols are important starting materials for the preparation of polyurethanes and polyesters. The purity of such diols is a critical factor in obtaining high-molecular-weight polymers. The present report deals with the continuous efforts to obtain nitro diols of highest purity.

2. Purification of 2-Nitro-2-methyl-1,3-propanediol

a. Discussion

(1) Purification of 2-nitro-2-methyl-1,3-propanediol via its isopropylidene derivative has been reported.* The isopropylidene

*Aerojet Report No. 638, p. 80.

derivative was prepared by treating the diol with acetone in benzene with an acid catalyst and with external removal of the water. This required about 2 full days reaction time. A new and much more rapid method with equally good yields has been developed. This is essentially the same as that reported for the preparation of the isopropylidene derivative of 2,2-dinitro-1,3-propanediol.* When one mole boron trifluoride etherate is added to one mole of 2-nitro-2-methyl-1,3-propanediol in 3 moles acetone, and within five to ten minutes the resulting mixture is poured into water, ice, and excess sodium bicarbonate, a 70% yield of the expected product, 2,2,5-trimethyl-5-nitro-1,3-dioxane, is obtained. This procedure has been applied on a large scale. The recrystallizations of the technical product yielded a material with 0.19 mole percent impurity.

(2) When the above dioxane derivative is hydrolyzed with dilute aqueous hydrochloric acid, the product, 2-nitro-2-methyl-1,3-propanediol, is isolated by evaporation to dryness. This material, when conveniently recrystallized from ethylene dichloride, still gives a positive test for chloride ion, thus indicating the presence of undesirable hydrochloric acid. The hydrochloric acid is not removed by repeated recrystallizations from ethylene dichloride but only by a relatively tedious recrystallization from ether or from mixed solvents such as benzene-ethanol. This problem has been relieved by replacing the hydrochloric acid in the hydrolysis mixture with an equivalent amount of trifluoroacetic acid. This material readily distills with water and traces of it are readily removed from the product by recrystallization from ethylene dichloride.

b. Experimental - Preparation of 2,2,5-Trimethyl-5-nitro-1,3-dioxane

A 500 ml flask was charged with 68 g (0.5 mole) tech. 2-nitro-2-methyl-1,3-propanediol and 75 ml acetone. Sixty-five ml (0.5 mole) tech. boron trifluoride etherate was added. Heat was evolved, and a homogeneous solution was formed. After 10 minutes, this solution was poured with good stirring into a mixture of 500 ml of saturated sodium bicarbonate solution and ice. The product was collected by filtration, washed well with cold water, and dried. The yield was 61 g (70% of theoretical), mp 83 to 84°C, completely soluble in warm hexane.

3. Preparation of 2,2-Dimethyl-5-hydroxymethyl-5-nitro-1,3-dioxane

a. Discussion

The isopropylidene derivative of nib-glycerol, 2,2-dimethyl-5-hydroxymethyl-5-nitro-1,3-dioxane, is a valuable intermediate

*Aerojet Report No. 663, p. 73.

desired for the urification of nib-glycerol, the preparation of 2,2-dinitro-1,3-propanediol, and the preparation of various amino derivatives via the Mannich reaction. Its preparation, as previously reported,* required a tedious filtration from finely divided calcium sulfate and gave about a 50% yield. Applying the method used for the isopropylidene derivatives of 2,2-dinitro-1,3-propanediol and 2-nitro-2-methyl-1,3-propanediol, one mole of nib-glycerol and one mole of boron trifluoride etherate in three moles acetone gave in a few minutes a 70% yield of the desired product.

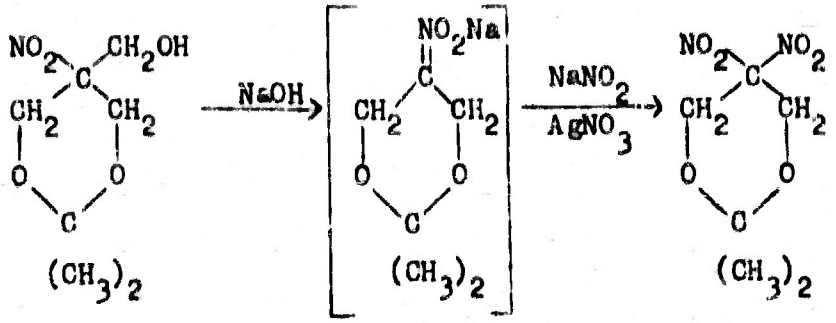
b. Experimental - Preparation of 2,2-Dimethyl-5-hydroxymethyl-5-nitro-1,3-dioxane

A one-liter flask was charged with 151 g (1 mole) of tech. tris-hydroxymethyl nitromethane and 220 ml (3 mole) acetone. The mixture was heated on a steam bath until all the nib-glycerol had dissolved, and was then cooled to 15 to 20°C. The nib-glycerol crystallized in fine needles. Boron trifluoride etherate (130 ml, 1 mole) was added with stirring. The temperature rose to 55°C and crystals of product began to appear. After 5 minutes, the mixture was poured as rapidly as possible into a stirred mixture of 1100 ml saturated sodium bicarbonate solution and ice. After stirring for 15 minutes the product was collected by filtration, washed well with cold water, and dried in vacuo. The yield was 137 g (72% of theoretical), mp 130 to 132°C. It was cream-colored and smelled slightly of mesityl oxide. Two larger runs (7 moles each) gave a 65% yield.

4. Preparation of 2,2-Dinitro-1,3-propanediol

a. Discussion

(1) It has previously been shown that for highest purity, 2,2-dinitro-1,3-propanediol must be purified via its isopropylidene derivative, 2,2-dimethyl-5,5-dinitro-1,3-dioxane.** This can be prepared from crude dinitropropanediol and acetone or by deformylation and oxidative nitration of 2,2-dimethyl-5-hydroxymethyl-5-nitro-1,3-dioxane.

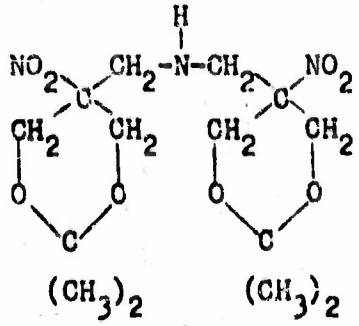


*Aerojet Report No. 622, p. 66.

**Aerojet Report No. 663, p. 71.

If this latter reaction, producing the desired acetone derivative, can be adapted directly to large scale, i.e., pilot-plant scale, it would be the preferred route. When a reaction such as this is expanded for larger scale a factor other than the yield of product assumes a greater importance, namely silver recovery. Thus, a method giving the highest yield of product with least manipulation of the silver precipitate is the best. With this in mind, several aspects of this method of preparation of dinitropropanediol have been investigated.

(2) It was previously shown that the addition of ammonia to the reaction mixture during the deformylation stage increased the yield from about 60 to 70%.* The presumed function of the ammonia was to tie up formaldehyde as hexamethylene tetramine, to make the deformylation irreversible. In one case in which the pH did not remain 11.0 or higher (see experimental section) a small amount of hexane-insoluble material melting at 182 to 184°C was isolated. This material analyzed well for the bis ammonia Mannich reaction product:



Since all subsequent procedures have avoided the particular conditions causing the formation of this impurity, no further difficulties along these lines are expected.

(3) Several runs on a one-mole scale have consistently given between 70 and 80% yields of crude product, using a methanol extraction to isolate the product. This yield is probably about maximum for this two-step reaction, and the principal problems remaining are those pertaining to the best isolation of product with least manipulation of silver. One difficulty which was readily overcome was that when the oxidative nitration was carried out in the usual way at 15 to 20°C, the silver precipitated in a very finely divided form, making the filtrations during the methanol extractions difficult. When the reaction temperature was raised to 45 to 50°C, the silver formed a coarse precipitate without the yield being adversely affected.

(4) The use of methanolic extraction of the product to separate it from precipitated silver requires several additional filtrations

*Aerojet Report No. 663.

or decantations from the silver. These manipulations are quite costly in terms of mechanical loss of silver. A method of separation which is probably the superior one is that in which benzene was added to the oxidative nitration reaction mixture after the oxidation. After vigorous stirring, this was filtered, and the product was isolated by steam distillation of the separated benzene layer. The product is extremely soluble in warm benzene and thus repeated extractions were not necessary. Second, only one filtration or manipulation of the silver was required. A yield of 68% of steam-distilled material was obtained.

b. Experimental

(1) A two-liter three-necked flask fitted with stirrer and thermometer was charged with 191 g (1.0 mole) 2,2-dimethyl-5-hydroxymethyl-5-nitro-1,3-dioxane and 400 ml water. With good stirring, 58 ml (1.1 mole) 50% sodium hydroxide solution was dropped in over about a half hour. When half the sodium hydroxide was added, the pH was 11.9. When all was in the pH was 11.8 and considerable material remained undissolved. Over about a half hour, 44.5 ml (0.667 mole) conc. ammonium hydroxide solution was dropped into the reaction mixture. Most of the remaining solid dissolved. The pH remained at 11.8. The mixture was warmed to 38°C for a half hour, at which time all was in solution except a small amount of brown gum. A solution of 75 g (1.0 mole) tech. sodium nitrite in 200 ml water was added and the mixture was filtered through glass wool. Water, 200 ml, was added and the solution was warmed to 42°C. With good stirring this was added as rapidly as possible to a solution of 340 g (2.0 mole) silver nitrate in 2.0 liters water at 43°C. The temperature rose to 51°C and a gray-black precipitate formed almost instantly. The mixture was stirred at 40°C for a half hour, cooled to room temperature, and filtered. The pH of the filtrate was 5.7. After it had been stirred for a half hour, 700 ml benzene was added and the mixture was stirred 20 minutes longer at 40 to 41°C. The mixture was filtered, and the silver was washed with additional benzene. The benzene layer was separated, concentrated, and then steam distilled. Benzene distilled first, followed by the product, which was collected and dried. The yield was 140 g (68%) colorless material, mp 54 to 55°C.

(2) Isolation of Ammonia Derivative

A deformylation was run in a similar manner to the above, except that 2.0 moles of sodium hydroxide instead of 1.1 mole was added. After the ammonia was added and the mixture was stirred 45 minutes, 1.0 mole of 6N nitric acid was added slowly with cooling. A semi-gelatinous precipitate formed. After the oxidative nitration the product was isolated by methanolic extraction. On attempting to purify the product by recrystallization from hexane, a hexane-insoluble portion was isolated in a yield of 3%. This consisted of colorless plates, mp 182 to 184°C. After it was recrystallized from methanol, then nitromethane, then methanol-dioxane, it was submitted for analysis; the mp was 182 to 184°C.

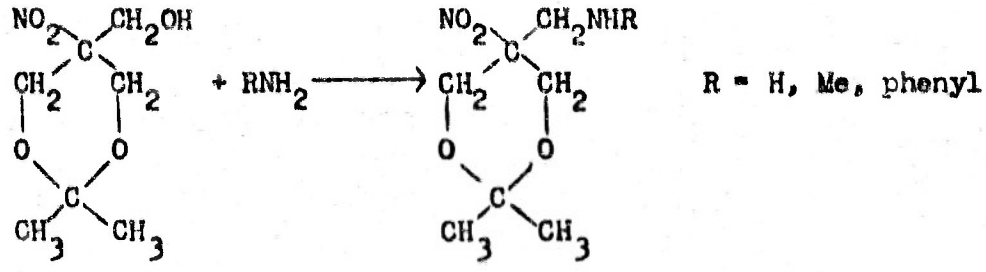
Anal. Calc'd for $C_{14}H_{25}N_3O_8$: %C, 46.27; %H, 6.94; %N, 11.56

Found: %C, 46.04; %H, 6.79; %N, 12.26

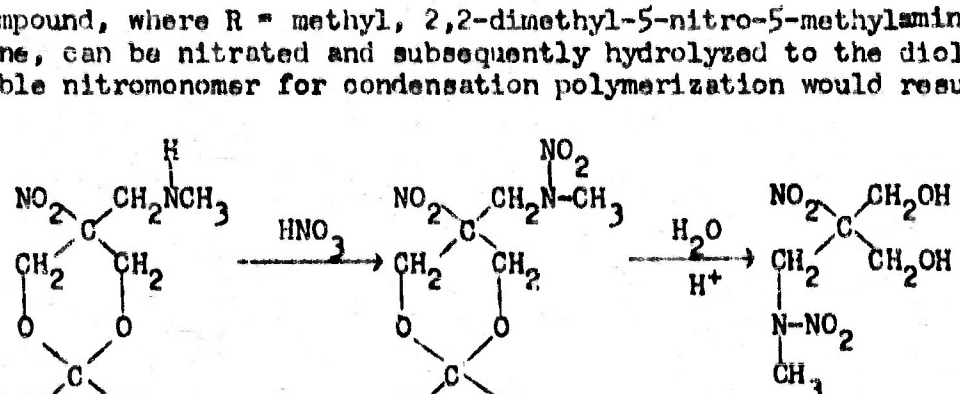
5. Attempted Preparation of 2-Nitro-2-(methyl-nitraminomethyl)-1,3-propanediol

a. Discussion

(1) It has recently been reported that 2,2-dimethyl-5-nitro-5-hydroxymethyl-1,3-dioxane can react in a Mannich reaction to yield the corresponding 5-aminomethyl derivatives:*



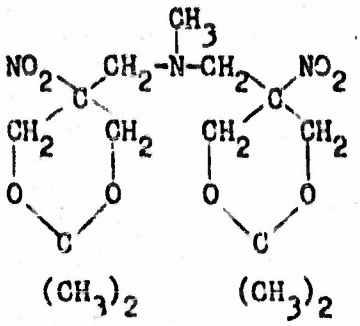
If the compound, where R = methyl, 2,2-dimethyl-5-nitro-5-methylaminomethyl-1,3-dioxane, can be nitrated and subsequently hydrolyzed to the diol, a new and valuable nitromonomer for condensation polymerization would result.



Obviously, if this synthesis is practical, numerous other useful monomers can be made using ethylene diamine, or ammonia, combining the synthesis with oxidative nitration steps.

(2) The abstract of the above-noted reference gives no experimental details. A photostat of the original article has been requested. In the meantime attempts have been made to prepare the desired methylamino derivative. Treatment of the hydroxymethyl compound with excess methyl ammonium acetate in concentrated aqueous solution at room temperature gave only starting material. At the boiling point, an oil soon separated, from which two compounds, mp 111 to 112°C and mp 243 to 245°C dec. were isolated. An elemental analysis of the compound melting at 111 to 112°C was in agreement with that of N,N-bis(1-nitro-4,4-dimethyl-3,5-dioxa-cyclohexyl-methyl) methylamine:

*S. Malinowski and T. Urbanski, Roczniki Chem. 25, 183-212 (1951); C.A. 46, 7993 (1952).



The reported melting point for the desired methylamino compound is 153°C; for its nitroso derivative, the mp is 111 to 112°C. The elemental analysis for the material melting at 243 to 245°C did not agree with that of any structure which could be reasonably postulated.

(3) The desired methylamino derivative was isolated when a solution of 2,2-dimethyl-5-nitro-5-hydroxymethyl-1,3-dioxane in aqueous methylamine was neutralized with acetic acid. Recrystallization from methanol gave a 35% yield of a material melting at 153 to 155°C. Its structure was confirmed by conversion to a nitroso derivative, mp 110 to 111°C. One attempt to nitrate this material yielded only water-soluble products. Other attempts will be made.

b. Experimental

(1) Preparation of 2,2-Dimethyl-5-nitro-5-methylaminomethyl-1,3-dioxane

A solution of 10 g (0.05 mole) of 2,2-dimethyl-5-nitro-5-hydroxymethyl-1,3-dioxane in 30 ml 40% aqueous methylamine was warmed to 40°C, cooled, and with cooling, neutralized with 25 ml glacial acetic acid. A finely divided precipitate formed. After dilution with water the product was isolated by filtration and recrystallized from boiling methanol. The yield was 3.5 g (35% of theoretical) of colorless plates, mp 153 to 155°C. Malinowsky and Urbanski reported a melting point of 153°C.

(2) Preparation of 2,2-Dimethyl-5-nitro-5-methylnitrosoaminomethyl-1,3-dioxane

A solution of 3.0 g (0.015 mole) of 2,2-dimethyl-5-nitro-5-methylaminomethyl-1,3-dioxane in 13 ml glacial acetic acid was stirred with 1.4 g (0.02 mole) sodium nitrite at room temperature for one hour. On dilution with ice water, a colorless precipitate formed, which was filtered, washed with water, and recrystallized from methanol, yielding 2.8 g (80%) of colorless needles, mp 111 to 112°C. Malinowsky and Urbanski reported a melting point of 111 to 112°C.

(3) Preparation of N,N-bis(1-Nitro-4,4-dimethyl-3,5-dioxacyclohexylmethyl) Methylamine and Unknown Material, mp 243 to 245°C

(a) A 500-ml three-necked flask fitted with mechanical stirrer and condenser was charged with 110 ml of 40% aqueous methylamine (1.2 mole). Water (150 ml) was added and, with cooling, glacial acetic acid was added until the pH reached 7 to 8. This required 73 ml acetic acid. To this solution was then added 46 g (0.24 mole) 2,2-dimethyl-5-nitro-5-hydroxymethyl-1,3-dioxane, and the mixture was heated to boiling and refluxed for one hour. The mixture became homogeneous before boiling started, and a few minutes later an oil began to separate. On cooling to about 50°C, the oil crystallized. The warm mixture was filtered and the solid was washed with water. The moist solid was warmed with 150 ml methanol which dissolved most of it. To the mixture was added 40 ml water and after heating again the solution was filtered; the solid was saved. The filtrate on cooling deposited needles which were isolated by filtration and recrystallized from 90:10 methanol-water to yield 19 g colorless needles, mp 111 to 112°C. Two more recrystallizations from methanol did not raise the melting point.

Anal. Calc'd for $C_{15}H_{27}N_3O_8$: %C, 47.74; %H, 7.21; %N, 11.13

Found: %C, 48.21; %H, 7.35; %N, 11.21

(b) The material in the above preparation which had been insoluble in aqueous methanol was recrystallized from nitromethane to yield 2.2 g colorless plates, mp 243 to 245°C dec. Two more recrystallizations from nitromethane did not raise the melting point.

Anal. Found: %C, 43.98; %H, 6.21; %N, 9.83

C. NITRO CARBOXYLIC ACIDS

1. Introduction

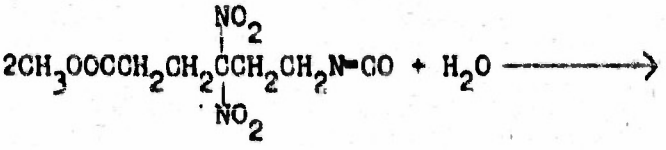
Nitro dicarboxylic acids are important intermediates for the preparation of diisocyanates and starting materials for the preparation of polyesters. This report describes the preparation of a new dicarboxylic acid containing a urea linkage.

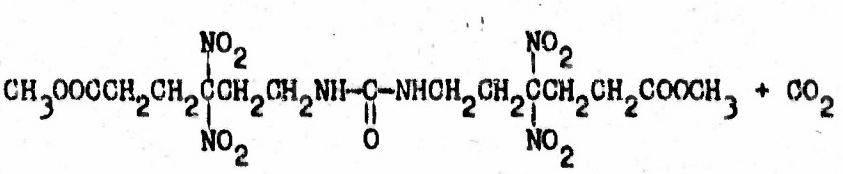
2. Preparation of Dimethyl 4,4,12,12-Tetranitro-7,9-diaza-8-keto-1,15-pentadecanedioate

a. Discussion

The physical properties of condensation and addition-type polymers depend on the structure of the starting monomers. Several types of nitrodicarboxylic acids containing gem dinitro groups, nitramino groups, or both of these, have been prepared. This report deals with the preparation

of a nitrodicarboxylic acid containing a urea group. The new compound, dimethyl 4,4,12,12-tetranitro-7,9-diaza-8-keto-1,15-pentadecanedioate, has been prepared by the reaction of 4,4-dinitro-6-carbomethoxyhexyl isocyanate with water, according to the equation:





It is planned to convert the new ester via the azide into the corresponding diisocyanate.

b. Experimental

A round-bottom flask was charged with 60 g 6-carbomethoxy-4,4-dinitrohexyl isocyanate and a mixture of 180 ml acetone and 60 ml water was added. The mixture warmed up immediately and was refluxed until the crystals precipitated. Upon cooling the whole mass solidified. The crystals were collected on a Buchner funnel, washed with water, and 60 g was recrystallized from acetone-water. A small amount was recrystallized from ethylene dichloride for analysis; the mp was 159 to 160°C.

Anal. Calc'd for $C_{15}H_{24}N_6O_{13}$: %C, 36.29; %H, 4.87; %N, 16.93; OCH_3, 12.51

Found: %C, 36.71; %H, 4.92; %N, 17.36; OCH_3, 12.12

3. Preparation of 4,7,10-Trinitro-4,7,10-triaza-1,13-tridecanedioyl Chloride

a. Discussion

The previous report described the preparation of 4,7,10-trinitro-4,7,10-triaza-1,13-tridecanedioic acid.* The preparation of larger quantities of this acid and work on the subsequent intermediates in the proposed synthesis of 3,6,9-trinitro-3,6,9-triaza-1,11-undecane diisocyanate have been hindered by the low yields encountered in the preparation of 4,7,10-trinitro-4,7,10-triaza-1,13-tridecane dinitrile (see

*Aerojet Report No. 663, p. 77.

Section V,E,1). However, a single attempt has been made on a small scale to convert the acid to the corresponding acid chloride. The acid chloride has been obtained only in an impure state.

b. Experimental

A mixture of 14.9 g (0.039 mole) 4,7,10-trinitro-4,7,10-triaza-1,13-tridecanedioic acid, 25 g (0.12 mole) phosphorous pentachloride, and 38 ml phosphorous oxychloride was warmed on the steam bath. Because there was no apparent solution of the acid after a brief heating period, an additional 62 ml phosphorous oxychloride was added, and heating was continued at gentle reflux temperature for a period of four hours. The product crystallized from solution as the latter cooled to room temperature. The acid chloride was collected by filtration and washed successively with dry carbon tetrachloride and absolute ether; the mp was 95 to 120°C. The product was recrystallized twice from 175 to 200-ml portions of hot, dry, ethylene dichloride to yield 8.7 g, mp 98 to 104°C.

D. NITRO ISOCYANATES

1. Introduction

Nitro isocyanates have been shown to be versatile starting materials for the preparation of polyurethanes and polyureas. They also serve as intermediates for the preparation of compounds containing functional groups. The present report describes an alternate procedure for the preparation of 3,3-dinitro-1,5-pentane diisocyanate in which the isolation of the hazardous azide is avoided. The isolation of 6-carbomethoxy-4,4-dinitrohexyl isocyanate is also reported.

2. Preparation of 3,3-Dinitro-1,5-pentane Diisocyanate

a. Discussion

The present method for the laboratory preparation of 3,3-dinitro-1,5-pentane diisocyanate involves the conversion of 4,4-dinitro-1,7-heptanedioyl chloride to the diisocyanate via the diazide.* The use of this method on a large scale produces serious safety hazards because of the danger involved in the handling of the solid dinitroheptanedioyl azide. A method has been devised which eliminates this hazard without sacrificing yield or quality of product. The method involves a heterogeneous reaction involving the addition of a chloroform solution of 4,4-dinitro-1,7-heptanedioyl chloride to an aqueous solution of sodium azide. The 4,4-dinitro-1,7-heptanedioyl azide is never present in the solid state but remains in the chloroform layer. The chloroform layer is separated, washed with water, and dried over sodium sulfate. The decomposition of the diazide and the isolation and purification of

*Aerojet Report No. 468, Appendix B, p. 1.

the 3,3-dinitro-1,5-pentane diisocyanate are then carried out in the established manner. It is quite probable that similar heterogeneous reactions can be applied to the preparation of other isocyanates.

b. Experimental

A solution of 28.7 g (0.1 mole) 4,4-dinitro-1,7-heptanedioyl chloride in 150 ml dry, alcohol-free chloroform was added in a fine stream to a solution of 19.5 g (0.3 mole) sodium azide in 50 ml water during a 5-min period, at 0 to 5°C. Stirring was continued for two hours at 0 to 5°C. The aqueous phase was separated, washed twice with 75-ml portions of chloroform, and washed a third time with 25 ml chloroform. These chloroform washes and the chloroform layer from the reaction mixture were combined, washed twice with 100 ml of water, and then dried over 40 g anhydrous sodium sulfate with stirring during a 15-min period. The drying agent was removed by filtration and washed with dry chloroform. A portion of the chloroform was distilled from the combined filtrates under diminished pressure to ensure complete removal of the water. The diazide was decomposed by warming the chloroform solution on the steam bath. In this latter process, the temperature was maintained sufficiently high to cause the continued distillation of the chloroform. The solution was distilled to near dryness. On chilling the residue, the crystalline diisocyanate precipitated. The mixture was diluted with absolute ether, and the product was separated by filtration and washed with a small amount of absolute ether. The diisocyanate was redissolved in absolute ether at 30 to 35°C. The product recrystallized on chilling this solution. The material was separated rapidly by filtration, washed with a small amount of absolute ether, and transferred to a vacuum desiccator over phosphorous pentoxide. When the product was thoroughly dried, an analysis was run which showed a purity of 98.4%. The 3,3-dinitro-1,5-pentane diisocyanate weighed 15.5 g, corresponding to 63.5% of the theoretical.

3. Preparation of 6-Carbomethoxy-4,4-dinitrohexyl Isocyanate

a. Discussion

Isocyanates containing functional groups are valuable intermediates for the preparation of multifunctional compounds. For example, monoisocyanates react with water giving ureas, thus doubling the molecule and forming a bifunctional compound. 6-Carbomethoxy-4,4-dinitrohexanoic acid* was converted into the 6-carbomethoxy-4,4-dinitrohexyl isocyanate according to the following series of equations:

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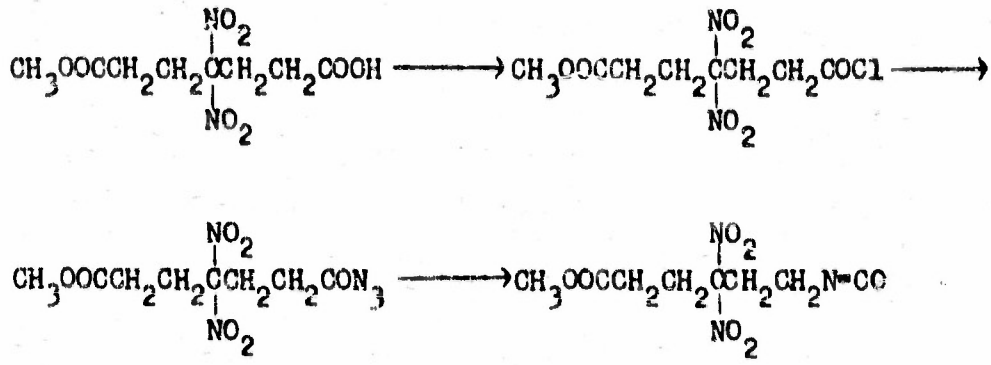
*Aerojet Report No. 622, p. 80.



The new isocyanate has already been converted into a dicarboxylic acid and will be used for the preparation of compounds suitable for the nitropolymer program and the coating of RDX.

b. Experimental

A round-bottom flask provided with a reflux condenser was charged with 500 ml thionyl chloride and 100 g 6-carbomethoxy-4,4-dinitrohexanoic acid. The mixture was refluxed for 3 hr. The excess of the thionyl chloride was then removed in vacuum. The yellow residue was dissolved in 100 ml acetone, and the acetone solution was dropped into a solution of 50 g sodium azide in 350 ml water with stirring. The addition took 15 minutes. The cloudy mixture was then stirred for 45 minutes at 20°C. The azide was extracted twice with 500 ml chloroform, and the chloroform solution was washed with water, 5% aqueous sodium bicarbonate, 5% aqueous sodium bisulfite, and water again. The solution was then dried over sodium sulfate and filtered. The solution of the azide was heated until decomposition started and refluxed for 60 minutes, and the chloroform was removed, leaving 60 g of 6-carbomethoxy-4,4-dinitrohexyl isocyanate. A small amount was distilled at 1 micron and 140 to 150°C airbath temperature, $n_D^{24} = 1.4793$.

Anal. Calc'd for $C_8H_{11}N_3O_7$: %C, 36.78; %H, 4.25; %N, 16.09

Found: %C, 37.37; %H, 4.58; %N, 16.46

E. INTERMEDIATES

1. Attempted Preparation of 4,7,10-Trinitro-4,7,10-triaza-1,13-tridecane Dinitrile

a. Discussion

The synthesis of 3,6,9-trinitro-3,6,9-triaza-1,11-undecane diisocyanate was proposed in the previous report.* Experimentally, the synthesis was carried as far as the preparation of 4,7,10-trinitro-4,7,10-triaza-1,13-tridecanedioic acid:

*Aerojet Report No. 663, p. 75.

$$HN(CH_2CH_2NH_2)_2 + 2CH_2{=}CHCN \longrightarrow HN(CH_2CH_2NHCH_2CH_2CN)_2 \longrightarrow$$

$$N(CH_2CH_2N(NO_2)CH_2CH_2CN)_2 \longrightarrow N(CH_2CH_2N(NO_2)CH_2CH_2CO_2H)_2$$

During the period covered by this report, efforts were made to improve the method of preparing 4,7,10-trinitro-4,7,10-triaza-1,13-tridecane dinitrile. Attempted nitrations of the tris-nitric acid salt of 4,7,10-triaza-1,13-tridecane dinitrile were made using anhydrous nitric acid-boron trifluoride, anhydrous nitric acid-boron trifluoride-chloride ion, and anhydrous nitric acid-boron trifluoride-chloride ion-acetic anhydride mixtures. Only the nitrating mixture containing acetic anhydride gave the desired 4,7,10-trinitro-4,7,10-triaza-1,13-tridecane dinitrile, but the yield was very low. The product was contaminated with a nitroso compound which gave an analysis indicating 4,10-dinitro-7-nitroso-4,7,10-triaza-1,13-tridecane dinitrile or 4,7-dinitro-10-nitroso-4,7,10-triaza-1,13-tridecane dinitrile as possible structures. On hydrolysis of the mixture of nitrated products the 4,7,10-trinitro-4,7,10-triaza-1,13-tridecanedioic acid was the sole product isolated. However, the overall yield of the acid from the tris-nitric acid salt of 4,7,10-triaza-1,13-tridecane dinitrile was only 17% of the theoretical.

b. Experimental

Following the addition of 5.5 ml boron trifluoride to 14 ml anhydrous nitric acid at 0 to 5°C, the cold solution was added dropwise with vigorous stirring to a mixture of 27 g of the tris-nitric acid salt of 4,7,10-triaza-1,13-tridecane dinitrile, 97 ml acetic anhydride, and 5.6 ml acetyl chloride at 20°C during a 10-min period. The mixture was stirred at 20°C for one hour, chilled to 0°C, and poured into an ice and water mixture. The precipitate was collected by filtration, washed successively with cold water, methanol, and absolute ether, and air-dried. The crude product weighed 15.7 g and melted at 85 to 120°C. The material was recrystallized from 200 ml acetone yielding Crop I (5.7 g, mp 126 to 137°C) on cooling the solution to room temperature. Crop II, 4.5 g, separated from the filtrate on the addition of absolute ether to turbidity. Crop III (1.5 g, mp 85 to 90°C) was obtained on the further addition of ether to the filtrate from Crop II. Crop III melted at 90 to 92°C following two recrystallizations from methanol. This material gave a positive Lieberman test for a nitroso group.

Anal. Calc'd for $C_{10}H_{16}N_8O_5$: %C, 36.58; %H, 4.90; %N, 34.14

Found: %C, 36.98; %H, 4.90; %N, 35.40

Possible formulae which correspond to the above data are 4,7-dinitro-10-nitroso-4,7,10-triaza-1,13-tridecane dinitrile and 4,10-dinitro-7-nitroso-4,7,10-triaza-1,13-tridecane dinitrile. The latter is the more probable structure.

2. Attempted Preparation of Di-(β-aminoethyl)-nitramine

Unsuccessful attempts to obtain 4,7,10-trinitro-4,7,10-triaza-1,13-tridecane dinitrile by direct nitration were described above. An alternate method for the synthesis of this compound is schematically shown below. This method proposed the preparation of di(β-aminoethyl)-nitramine (III) which on cyanoethylation and subsequent nitration would yield 4,7,10-trinitro-4,7,10-triaza-1,13-tridecane dinitrile (V), according to the equation:

$$2C_6H_5CHO + NH(CH_2CH_2NH_2)_2 \longrightarrow NH(CH_2CH_2N{=}CHC_6H_5)_2$$
(I)

$$(I) \longrightarrow N(NO_2)(CH_2CH_2N{=}CHC_6H_5)_2 \longrightarrow N(NO_2)(CH_2CH_2NH_2)_2$$
(II) (III)

$$(III) + 2CH_2{=}CHCN \longrightarrow N(NO_2)(CH_2CH_2NHCH_2CH_2CN)_2 \longrightarrow N(NO_2)(CH_2CH_2N(NO_2)CH_2CH_2CN)_2$$
(IV) (V)

The Schiff base was obtained as a waxy product, mp 47 to 52°C, insoluble in water. No suitable solvent was found for recrystallization. Upon attempting to isolate the nitric acid salt, the tris-nitric acid salt of diethylene triamine was obtained as a result of the hydrolysis of the Schiff base.

3. Attempted Preparation of Di-(β-cyanoethyl)-nitramine

a. Discussion

Calculation of the specific impulse of 3-nitro-3-aza-1,5-pentane diisocyanate, and more important, the specific impulse of the postnitrated polymer with 2,2-dinitro-1,3-propanediol, show that this monomer would be very desirable from the standpoint of high energy. The polymer of the diisocyanate with 2,2-dinitro-1,3-propanediol has a calculated specific impulse of 167 lbf-sec/lbm, and the postnitrated polymer has a calculated specific impulse of 215 lbf-sec/lbm. The proposed synthesis of 3-nitro-3-aza-1,5-pentane diisocyanate (VI) is schematically outlined below:

$$2CH_2{=}CHCN + NH_3 \longrightarrow HN(CH_2CH_2CN)_2 \longrightarrow N(NO_2)(CH_2CH_2CN)_2$$
(I) (II)

$$\longrightarrow N(NO_2)(CH_2CH_2CO_2H)_2 \longrightarrow \cdots\cdots \longrightarrow N(NO_2)(CH_2CH_2NCO)_2$$
(III) (VI)

Di-(β-cyanoethyl)-amine (I) was prepared by the addition of acrylonitrile to aqueous ammonia in much the same manner as used by Bue, Ford, and Wise* and Wiedemann and Montgomery.** The attempted conversion of this product to di-(β-cyanoethyl)-nitramine (II) using an anhydrous nitric acid-acetic anhydride mixture containing a chloride catalyst gave only water-soluble products. A similar nitration was carried out using di(β-carboxyethyl)-amine hydrochloride. The replacement of the cyano groups with carboxyl groups was expected to yield a less basic amine with a greater probability of successful nitration. Unfortunately, this nitration also yielded water-soluble products. The di-(β-carboxyethyl)-amine hydrochloride was obtained by the hydrolysis of di-(β-cyanoethyl)-amine in concentrated hydrochloric acid.

b. Experimental

(1) Preparation of Di-(β-cyanoethyl)-amine

Acrylonitrile (530 g; 10 moles) was added dropwise at 20 to 25°C to 695 ml (5 moles) 28% aqueous ammonia during a 15 to 20-min period. When addition of the acrylonitrile was complete, the temperature of the reaction mixture began to rise, and external cooling was required to maintain the temperature below 30°C. Less cooling was required as the reaction proceeded. After a 3-hr period of stirring at 25 to 30°C, the solution was warmed at 40°C for 30 minutes. The water was distilled under reduced pressure, and the following data were taken during the distillation of the product.

Cut I: bp 90-154°C/0.5 mm; 63.2 g; n_D^{25} 1.4550

Cut II: bp 154-156°C/0.5 mm; 430 g; n_D^{25} 1.4620.

Cut III: bp 154°C/0.5 mm; 52 g; n_D^{25} 1.4625

Residue: 23 g

Cuts II and III correspond to a 78.4% yield of di-(β-cyanoethyl)-amine. The nitric acid salt, mp 133 to 135°C, was prepared by the addition of nitric acid to a cold solution of a sample of Cut II in ethanol. This salt was quite water-soluble.

(2) Preparation of Di-(β-carboxyethyl)-amine Hydrochloride

Di-(β-cyanoethyl)-amine (123 g; 1 mole) was added dropwise with stirring to 250 ml (3 moles) concentrated hydrochloric acid while the temperature was held below 40°C by external cooling. The resulting solution was rapidly heated to 95°C on the steam bath. Without further

*J. Am. Chem. Soc. 67, 92 (1945).

**J. Am. Chem. Soc. 67, 1994 (1945).

heating, the temperature rose to 115 to 120°C. During a 15-min period, the temperature of the solution dropped to 100°C with the precipitation of a white solid. An additional 38 ml (0.46 mole) concentrated hydrochloric acid was added, and stirring was continued for 18 hr while the temperature was maintained at 90 to 95°C by means of the steam bath. Stirring became difficult with the precipitation of additional solid as the mixture was cooled to room temperature. The solid was collected on a sintered-glass Buchner funnel and washed successively with 500-ml portions of acetone and absolute ether. After thorough drying in a vacuum desiccator over potassium hydroxide, the crude di-(β-carboxyethyl)-amine hydrochloride weighed 216.5 g (theoretical yield, 197.6 g). The material was contaminated with ammonium chloride. As attempts to purify samples of the hydrochloride by extraction with hot absolute ethanol or isopropanol were unsatisfactory, the material was not further purified. The structure of the crude product was verified by conversion to di-(β-carboxyethyl)-nitrosamine.

4. Attempted Preparation of 4,6-Diaza-1,9-nonane Dinitrile

Two unsuccessful attempts to carry out the Michael reaction involving methylene diamine and acrylonitrile were conducted in order to prepare 4,6-diaza-1,9-nonane dinitrile (I), an intermediate for the proposed synthesis of 3,5-dinitro-3,5-diaza-1,7-heptane diisocyanate (VI):

$$2CH_2{=}CHCN + CH_2(NH_2)_2{\cdot}2HCl \xrightarrow{\text{Base}} CH_2(NHCH_2CH_2CN)_2$$

(I)

$$\longrightarrow CH_2(\overset{NO_2}{\overset{|}{N}}CH_2CH_2CN)_2 \longrightarrow CH_2(\overset{NO_2}{\overset{|}{N}}CH_2CH_2CO_2H)_2$$

(II) (III)

$$\longrightarrow CH_2(\overset{NO_2}{\overset{|}{N}}CH_2CH_2COCl)_2 \longrightarrow CH_2(\overset{NO_2}{\overset{|}{N}}CH_2CH_2CON_3)_2 \longrightarrow CH_2(\overset{NO_2}{\overset{|}{N}}CH_2CH_2NCO)_2$$

(IV) (V) (VI)

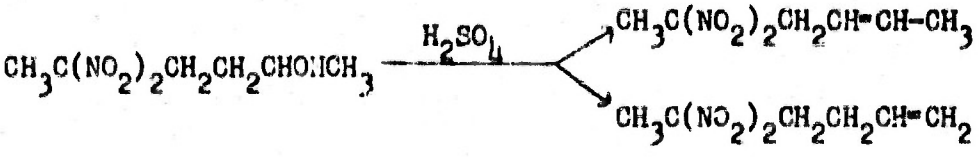
The only product isolated from the initial reaction was di-(β-cyanoethyl)-amine. This material evidently results from the degradation of the methylene diamine to ammonia followed by the Michael addition of two moles of acrylonitrile with the ammonia. Further work on this problem will be postponed until a later date, although the eventual preparation of the diisocyanate is desirable.

The polymer prepared from 3,5-dinitro-3,5-diaza-1,7-heptane diisocyanate and 2,2-dinitro-1,3-propanediol has a calculated specific impulse of 187.8 lbf sec/lbm, and the postnitrated polymer has a calculated specific impulse of 227.9 lbf sec/lbm.

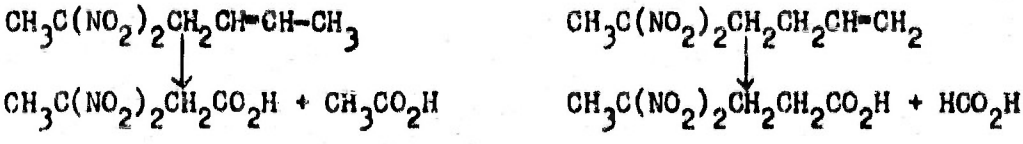
5. Preparation of 5,5-Dinitro-2-hexene

a. Discussion

(1) Treatment of 5,5-dinitro-2-hexanol with sulfuric acid yielded a hexane-soluble oil with the properties of dinitrohexene.* The position of the double bond in this compound was not completely established, as it could be either a 1- or a 2-hexene:



That this compound is at least principally the 5,5-dinitro-2-hexene has now been conclusively established by the isolation of the new 3,3-dinitrobutyric acid upon oxidation with permanganate. 5,5-Dinitro-1-hexene would give the known 4,4-dinitrovaleric acid:



The yield of 5,5-dinitro-2-hexene from 5,5-dinitro-2-hexanol (originally reported as 29%) has been raised to 66% when the reaction was conducted using slightly larger quantities. The oxidation is described in Section V,A,3.

(2) The success of the above oxidation indicates that the 5,5,5-trinitropentene isolated by dehydration of 5,5,5-trinitro-2-pentanol with sulfuric acid,** is undoubtedly 5,5,5-trinitro-2-pentene. It likewise indicates that the currently unknown 3,3,3-dinitropropionic acid might be readily available from the permanganate oxidation of this 5,5,5-trinitro-2-pentene or the 4,4,4-trinitro-1-butene recently available from silver nitroform and allyl bromide.*** These oxidations will be attempted when time permits.

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*Aerojet Report No. 638, p. 77.

**Aerojet Report No. 622, p. 71.

***Rohm & Haas Co., Quarterly Progress Report P-52-1, June, 1952; Quarterly Progress Report P-52-3, September, 1952.

b. Experimental - Preparation of 5,5-Dinitro-2-hexene

Five drops of conc. sulfuric acid was added to a 4.0-g portion of 5,5-dinitro-2-hexanol in a 6-in. test tube. The solution was boiled (behind a safety shield) over a free flame until a second black phase developed. This required about 40 seconds. Eight such runs were combined and extracted with hexane. The hexane solution was washed with water, dried, and evaporated through a 15-in. glass-helices-packed column at atmospheric pressure and then at water pump pressure at 30°C. The residue, 25 g, was distilled at 1 to 2 mm, yielding a 0.5-g forerun, n_D^{25} 1.4554, and 19 g of colorless product (66% of theoretical), bp 59 to 60°C, n_D^{25} 1.4557.

6. 4,4-Dinitrovaleraldehyde from Oxidation of 5,5-Dinitro-1,2-hexanediol

a. Discussion

The structure of 5,5,5-trinitro-1,2-pentanediol was confirmed by oxidation with periodic acid to give 4,4,4-trinitrobutanal.* This oxidation has now been run with 5,5-dinitro-1,2-hexane-diol** to yield 4,4-dinitrovaleraldehyde, identical with that reported by H. Shechter et al. from dinitroethane and acrolein.***

b. Experimental

A solution of 20.5 g (0.09 mole) periodic acid, H_5IO_6, in 90 ml water was added over 10 minutes to a solution of 16 g (0.075 mole) 5,5-dinitro-1,2-hexanediol in 80 ml water at 23 to 25°C. The separated oil was taken up in methylene chloride. The solution was washed with water, dried over Drierite, and evaporated to dryness, leaving 13.5 g of crude dinitropentanal, n_D^{25} 1.4641. A sample was twice distilled in a bulb tube at 80 to 90°C and 5μ to yield a colorless oil, n_D^{25} 1.4640.

Anal. Calc'd for $C_5H_8N_2O_5$: %C, 34.09; %H, 4.58; %N, 15.91

Found: %C, 34.24; %H, 4.51; %N, 15.78

The 2,4-dinitrophenylhydrazone gave yellow plates from ethanol-dioxane, mp 137 to 138°C.

Anal. Calc'd for $C_{11}H_{12}N_6O_8$: %N, 23.59

Found: %N, 23.88

*Aerojet Report No. 563, p. 79.

**Aerojet Report No. 638, p. 85.

***Ohio State University Report No. 3, October, 1950, p. 10.

7. Preparation of 5-Nitro-1,3-dioxanes

a. Discussion

The method of preparing the acetone derivatives of 1,3-diols, using excess acetone with one mole of diol and one mole of boron trifluoride etherate, as exemplified by 2-nitro-2-methyl-1,3-propanediol, nib glycerol, and 2,2-dinitro-1,3-propanediol,* seems to be of general applicability; and it appeared of interest to determine whether the scope of the reaction could be broadened. In the case of water-insoluble aldehydes and ketones where excess reagent would interfere with isolation of product, the reaction is successfully run in acetonitrile with only a small excess of carbonyl compound. Paraformaldehyde was successfully used as a source of formaldehyde in acetonitrile. The reaction was also successfully applied to a nitro diol containing an active hydrogen, 2-nitro-1,3-propanediol.

b. Experimental - Preparation of 2-Methyl-2,5-diethyl-5-nitro-1,3-dioxane

A 200-ml Erlenmeyer flask was charged with 15 g (0.1 mole) 2-nitro-2-ethyl-1,3-propanediol, 8 g (0.11 mole) methyl ethyl ketone, 20 ml acetonitrile and 13 ml (0.1 mole) boron trifluoride etherate. Heat was evolved and all dissolved. The solution was warmed for 10 minutes on a steam bath and poured into a mixture of 9 g sodium bicarbonate, 80 ml water, and excess ice. The precipitated oil was taken up in methylene chloride and dried over Drierite. Evaporation to dryness left 15 g of a light-tan oil which could not be crystallized. It was distilled at reduced pressure to yield 11 g (50%) of a colorless middle cut, n_D^{25} 1.4571, bp 65 to 70°C at 0.5μ. A small sample was redistilled in a bulb tube as above to yield a middle cut, n_D^{25} 1.4569, which was submitted for analysis.

Anal. Calc'd for $C_9H_{17}NO_4$: %C, 53.18; %H, 8.43; %N, 6.89

Found: %C, 52.11; %H, 8.27; %N, 7.27

(2) Preparation of 5-Methyl-5-nitro-1,3-dioxane

A 200-ml flask was charged with 13.5 g (0.1 mole) 2-nitro-2-methyl-1,3-propanediol, 4 g (0.13 mole) paraformaldehyde, 20 ml acetonitrile, and 13 ml (0.1 mole) boron trifluoride etherate. All dissolved rapidly except the paraformaldehyde. The mixture was boiled for 5 minutes on a steam bath, at which time the paraformaldehyde had disappeared. The solution was poured into 9 g sodium bicarbonate, 80 ml water, and excess ice. A crystalline solid precipitated. This was washed with ice water and dried *in vacuo* to yield 12 g, mp 67 to 69°C. Recrystallization from aqueous methanol

*Aerojet Report No. 663, p. 72.

gave 11 g (73%), mp 70 to 71°C. Senkus has reported a melting point of 71°C.* A sample was recrystallized from aqueous methanol then from ethanol and submitted for analysis.

Anal. Calc'd for $C_5H_9NO_4$: %C, 40.81; %H, 6.17; %N, 9.52

Found: %C, 40.81; %H, 6.17; %N, 9.84

(3) Preparation of 2,2-Dimethyl-5-nitro-1,3-dioxane

The addition of 6.5 ml (0.05 mole) of boron trifluoride etherate to a solution of 6.0 g (0.05 mole) of mononitropropanediol in 12 ml acetone caused the evolution of heat and darkening. After 10 minutes, the solution was poured into 60 ml 1N sodium bicarbonate and ice. The crystalline solid was washed with ice water and air-dried to yield 3.1 g (37%), mp 60 to 61°C. A sample was recrystallized from aqueous methanol and then hexane to yield colorless plates, mp 60 to 61°C.

Anal. Calc'd for $C_6H_{11}NO_4$: %C, 44.71; %H, 6.88; %N, 8.69

Found: %C, 45.32; %H, 6.78; %N, 8.52

8. Reaction of Halo Nitro Compounds with Metals

a. Discussion

(1) As reported previously,** the Michael reaction of chloronitro compounds with methyl acrylate was undertaken to provide intermediates for the preparation of unsaturated nitro compounds and bifunctional nitro compounds. While removal of halogen and formation of a double bond failed, the reaction with metals was studied in order to prepare bifunctional nitro compounds. However, this reaction also failed, but it has been observed previously that methyl 4-nitro-4-chloropentanoate and zinc metal reacted rapidly, with the formation of a white precipitate of unknown structure. This white compound was found to be insoluble in water and in all common organic solvents, thereby making purification impossible. It was found that the white precipitate contained zinc, and it reacted with dilute mineral acids with the formation of methyl 4-keto-pentanoate. When 1-bromo-1-nitrocyclohexane was used the white precipitate gave cyclohexanone upon treatment with hydrochloric acid. Methyl 4-chloro-4-nitrohexanoate was converted into methyl 4-ketohexanoate.

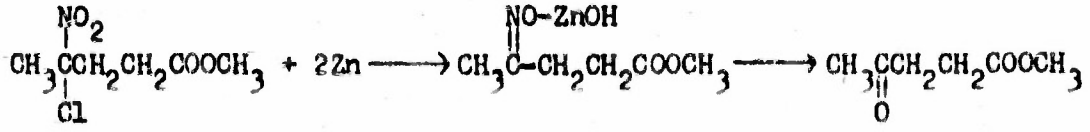
(2) Zinc metal reacts with aliphatic nitro compounds to form hydroxyl amines.*** No information is available regarding the reaction

*J. Am. Chem. Soc. 63, 2635 (1941).

**Aerojet Report No. 482, p. 11.

***Bamberger, Ber. 27, 1350 (1894); Majert, Ann. 362, 204 (1909).

of zinc and halo nitro compounds. The analysis of the crude white precipitate is inconclusive, because the white precipitate in some cases is halogen-free, and in other cases contains some halogen. Since treatment of the white precipitate with mineral acid gave ketones, the following explanation for formation and structure is proposed:



This structure would explain the ratio of the reactants, the formation of an insoluble metal complex containing nitrogen, and the easy conversion of the metal complex into methyl 4-keto-valerate upon treatment with mineral acid.

(3) Other compounds react in the same ratio with Zn as reported for methyl 4-nitro-4-chlorovalerate. For example, 2-chloro-2-nitropropane forms a white precipitate in fair yield with zinc, 1-bromo-1-nitrocyclohexane reacts rapidly in 10% alcohol solution and without solvent in an almost explosive manner; and methyl 4-chloro-4-nitrohexanoate forms a white precipitate in good yield. Gem dinitro compounds, such as 3,3-dinitropentane dimethyl urethane or 3,3-dinitro-1,5-pentane diamine dihydrochloride also react in the same manner. However, since this work did not proceed in the desired direction, no further effort is planned along these lines.

b. Experimental

(1) Methyl 4-Nitro-4-chlorovalerate and Zinc

(a) A three-necked flask provided with a thermometer, stirrer, and reflux condenser was charged with 19.6 g methyl 4-nitro-4-chlorovalerate, 100 ml methanol, 10.2 g zinc dust and 5 g ammonium chloride. The mixture was stirred vigorously. The temperature rose to 48°C and a white precipitate was formed. The mixture was kept stirring for 10 minutes at 60°C until all zinc metal was consumed. The mixture was then cooled, and the precipitate was collected and washed with methanol and ether. The yield was 18 g of white crystals carrying a high electric charge, analyzed without further purification.

Anal. Calc'd for $C_6H_{11}NO_4Zn$: %C, 31.81; %H, 4.90; %N, 6.18; %Zn, 28.86

Found: %C, 32.48; %H, 3.82; %N, 6.11; %Zn, 22.81

(b) Hydrolysis

Ten g of the dry white precipitate was suspended in 100 ml water, and hydrochloric acid was added. The precipitate dissolved quickly to form a blue solution, from which an oil suddenly

separated. The oil was extracted and distilled in a bulb tube at 80°C air-bath temperature and 5 mm pressure.

Anal. Calc'd for $C_5H_{10}O_3$: %C, 55.37; %H, 7.74; %OCH_3, 24.40

Found: %C, 55.51; %H, 7.79; %OCH_3, 23.29

(c) Identification

Two grams of the oil obtained under (b) was treated with a filtered solution of 3 g semicarbazide hydrochloride and 3 g sodium acetate in 70 ml methanol. After evaporation of the solvent a crystalline compound was obtained, which after recrystallization from water had a melting point of 148 to 149°C. The mixed melting point with methyl 4-ketopentanoate was not depressed.

Anal. Calc'd for $C_7H_{13}O_3N_3$: %C, 44.91; %H, 7.00; %N, 22.45

Found: %C, 45.31; %H, 7.09; %N, 21.78

(2) 1-Bromo-1-nitrocyclohexane and Zinc

(a) A three-necked flask provided with a stirrer, thermometer, and reflux condenser was charged with 20.8 g bromo-nitrocyclohexane, 10.2 g zinc dust, 10 g ammonium chloride, and 250 ml methanol. The temperature rose to 45°C and a white precipitate was formed instantly. After 10 minutes refluxing all zinc metal was consumed. The mixture was cooled, and the precipitate was collected and dried in a desiccator. The yield was 18 g.

Anal. Found: %C, 30.27; %H, 5.17; %N, 9.39; %Br, 22.04.

(b) Hydrolysis

Ten g of the precipitate was suspended in 100 ml water, and hydrochloric acid was added. The precipitate dissolved and cyclohexanone odor was noticeable. The water phase was extracted with ether, and the ether was removed. The yield was 5.2 g. This oil was converted into the semicarbazone by treating it with a clear solution of 5 g semicarbazide hydrochloride and 5 g sodium acetate in 100 ml methanol. The semicarbazone formed had a melting point of 169 to 170°C after recrystallization from water. The mixed melting point with cyclohexanone semicarbazone was not depressed.

9. 2-Nitro-1-propyl p-Toluenesulfonate

a. This new compound was reported to melt at 74 to 75°C.* It has now been purified and analyzed.

*In Aerojet Report No. 663, p. 69.

b. A sample was prepared as previously described. It was recrystallized from methanol, then from isopropanol, from benzene-cyclohexane, and finally from isopropanol to yield colorless chunky plates, mp 77 to 78°C.

Anal. Calc'd for $C_{10}H_{13}NO_5S$: %N, 5.40; %S, 12.37

Found: %N, 5.16; %S, 12.37

10. 4,4,4-Trinitrobutanal

a. The 2,4-dinitrophenylhydrazone of this aldehyde was reported previously.* It has been purified and analyzed.

b. The original sample (0.8 g) was recrystallized twice from absolute ethanol (50 to 70 ml) yielding fine yellow needles, mp 162 to 163°C.

Anal. Calc'd for $C_{10}H_9N_7O_{10}$: %N, 25.32

Found: %N, 25.05

F. NITROSAMINES

1. Introduction

In comparison with the high-energy nitramino group, the nitrosamino group does not make an outstanding contribution to the specific impulse of a given compound. Consequently, the nitrosamines are not particularly interesting for use in nitropolymer work. However, the nitrosamines are readily available from the free amine or amine salts by the action of nitrous acid, and the development of a general method for their conversion to nitramines would make a number of highly desirable nitramines available which, at present, cannot be prepared by other means. The preparation of three nitrosamines - 4,7,10-trinitroso-4,7,10-triaza-1,13-tridecane dinitrile, di-(β-carboxyethyl)-nitrosamine, and di-(β-cyanoethyl)-nitrosamine - is described in this report. A series of attempts to oxidize di-(β-cyanoethyl)-nitrosamine and 4,7-dinitroso-4,7-diaza-1,10-decane dinitrile to the corresponding nitramines are also described.

2. Preparation of 4,7,10-Trinitroso-4,7,10-triaza-1,13-tridecane Dinitrile

a. Discussion

4,7,10-Trinitroso-4,7,10-triaza-1,13-tridecane dinitrile was prepared from the tris-nitric acid salt of 4,7,10-triaza-1,13-tridecane dinitrile by the action of nitrous acid. This nitrosation was carried

*In Aerojet Report No. 563, p. 79.

out for the purpose of assaying the nitric acid salt. The very low yields which had been obtained in the nitration of this salt* suggested that it possibly existed as an isomeric mixture. The nearly quantitative yield (94.8%) of the trinitroso derivative verified the purity of the salt.

b. Experimental

A solution of 119.4 g (0.3 mole) tris-nitric acid salt of 4,7,10-triaza-1,13-tridecane dinitrile in 400 ml water was prepared by warming the mixture to 90°C. The solution was acidified with 2 ml concentrated hydrochloric acid, and a solution of 69 g (0.969 mole) 97% sodium nitrite in 100 ml water was added in a fine stream. Sufficient heat was evolved to maintain the temperature at 90°C during the 5 to 10-min period of addition. Additional hydrochloric acid (ca 5 ml, added in increments) was required to maintain the reaction mixture on the acid side. The mixture was warmed at 90 to 95°C with continuous stirring for two hours. The product layer solidified when the mixture was chilled to 0°C. The product was collected by filtration and recrystallized from 2875 ml methanol. After drying in a vacuum desiccator over phosphorous pentoxide, the 4,7,10-trinitroso-4,7,10-triaza-1,13-tridecane dinitrile, mp 87.5 to 89°C, weighed 84.6 g, corresponding to 94.8% of the theoretical yield. A purified sample, mp 90 to 92°C, was prepared for analysis by successive recrystallizations from methanol and ethyl acetate.

Anal. Calc'd for $C_{10}H_{16}N_8O_3$: %C, 40.53; %H, 5.44; %N, 37.82

Found: %C, 40.43; %H, 5.40; %N, 37.00

3. Preparation of Di-(β-carboxyethyl)-nitrosamine

a. Discussion

Di-(β-carboxyethyl)-nitrosamine was prepared for the purpose of establishing the structure of di-(β-carboxyethyl)-amine hydrochloride. The latter was obtained by the hydrolysis of the corresponding dinitrile and was contaminated with ammonium chloride (Section V,E,3). Because this mixture was not readily separable, and it gave no water-insoluble product on attempted conversion to di-(β-carboxyethyl)-nitramine by nitration, the presence of the di-(β-carboxyethyl)-amine hydrochloride was proved by conversion to the nitroso derivative.

b. Experimental

A solution of 66 g (1/3 mole) crude di-(β-carboxyethyl)-amine hydrochloride in 50 ml water was heated to 90°C, 1 ml concentrated hydrochloric acid was added, and a solution of 23 g (0.323 mole) 97% sodium

*Aerojet Report No. 663, p. 76.

nitrite in 35 ml water was added at 90 to 95°C during a 10-min period. A small additional quantity of concentrated hydrochloric acid was required to maintain the pH of the solution on the acid side. Stirring was continued for 1-1/4 hr while the temperature was held at 90 to 95°C. When the solution was chilled to 0 to 5°C, 4 g white solid separated, which was identified as ammonium chloride. The filtrate was extracted three times with 100-ml portions of ethyl acetate. The combined extracts were dried over anhydrous sodium sulfate and distilled in vacuo. The 14-g solid residue melted at 92 to 94°C. The continuous extraction of the reaction solution with ethyl acetate for a 21-hr period yielded an additional 9.5 g of product. The 23.5-g yield corresponded to 37.1% of the theoretical, on the basis of pure di-(β-carboxyethyl)-amine hydrochloride. Three recrystallizations of a sample of the di-(β-carboxyethyl)-nitrosamine from ethyl acetate gave a purified material, mp 96.5 to 97.5°C.

Anal. Calc'd for $C_6H_{10}N_2O_5$: %C, 37.89; %H, 5.30; %N, 14.74

Found: %C, 37.77; %H, 5.34; %N, 14.76

4. Preparation of Di-(β-cyanoethyl)-nitrosamine

a. Discussion

Di-(β-cyanoethyl)-nitrosamine was prepared in 89% yield by the action of nitrous acid on di-(β-cyanoethyl)-amine. This nitrosamine was desired for use as a model in oxidation experiments with the purpose of developing a process for the preparation of nitramines.

b. Experimental

Concentrated hydrochloric acid (50 ml, 0.6 mole) was added dropwise with stirring to 74 g (0.6 mole) di-(β-cyanoethyl)-amine while maintaining the temperature below 80°C. A suspension of 46 g (0.646 mole) 97% sodium nitrate in 40 ml water was added during a 15-min period. The temperature was maintained at 80 to 85°C without external heating. Additional hydrochloric acid was required following the complete addition of the sodium nitrite. Stirring was continued for 30 min while the temperature was held at 90 to 95°C by means of the steam bath. When the reaction mixture was chilled to 0 to 5°C, the product layer crystallized. The solid was separated by filtration and pressed as dry as possible. Recrystallization from 600 ml methanol followed by thorough drying over phosphorous pentoxide in a vacuum desiccator yielded 81.3 g di-(β-cyanoethyl)-nitrosamine, mp 46 to 46.5°C, corresponding to 89% of the theoretical. Three recrystallizations of a sample of the product from methanol did not alter the melting point.

Anal. Calc'd for $C_6H_8N_4O$: %C, 47.36; %H, 5.30; %N, 36.83

Found: %C, 47.64; %H, 5.45; %N, 37.42

5. Attempted Conversion of Nitrosamines to Nitramines

The value of a general method for converting nitrosamines to nitramines has become exceedingly apparent with unsuccessful or unsatisfactory attempts to obtain di-(β-cyanoethyl)-nitramine, di-(β-carboxyethyl)-nitramine, and 4,7,10-trinitro-4,7,10-triaza-1,13-tridecane dinitrile by direct nitration. On the other hand, the corresponding nitrosamines were readily obtained by the action of nitrous acid. A number of experiments have been carried out on 4,7-dinitroso-4,7-diaza-1,10-decane dinitrile* and di-(β-cyanoethyl)-nitrosamine in attempts to oxidize these nitrosamines to the corresponding nitramines. 4,7-Dinitroso-4,7-diaza-1,10-decane dinitrile was chosen as one model for these experiments, as the corresponding nitro compound and nitro dicarboxylic acid have been characterized.** Di-(β-cyanoethyl)-nitrosamine was used as the second model because of its simpler structure. Thus far all attempts to oxidize the nitrosamines have been unsuccessful. The results of these tests are given in Tables XXXII and XXXIII.

VI. SPIA DATA

A Solid Propellant Information Agency data sheet has been compiled for polyurethane I-J, from 2-nitro-2-methyl-1,3-propanediol and 3,3-dinitro-1,5 pentane diisocyanate, and is presented as Appendix A.

*Aerojet Report No. 638, p. 89.
**Ibid.

TABLE XXXII

ATTEMPTED OXIDATION OF 4,7-DINITROSO-4,7-DIAZA-1,10-DECANE DINITRILE

Dinitroso Comp'd g	Solvent-Reagent	Conditions: Temp, °C	Conditions: Time	Product
5	25 ml 100% HNO_3, 25 ml H_2SO_4	50-5	15 min	
5	25 ml 100% HNO_3, 25 ml H_2SO_4	75-80	15 min	
5	50 ml 100% HNO_3	25	30 min	Water-soluble products
2	20 ml 100% HNO_3	60-5	10 min	
2	20 ml 70% HNO_3	90	15 min	
5	50 ml 100% HNO_3, 12.2 g $(NH_4)_2S_2O_8$	0	1 hr	
22.4	13.8 ml 100% HNO_3, 94.5 ml $(CH_3CO)_2O$, 2.8 ml CH_3COCl	20	22 hr	
1	10 ml CH_3CO_2H, 10% excess 30% H_2O_2	25	48 hr	
1	10 ml CH_3CO_2H, 10% excess 30% H_2O_2, 0.5 ml H_2SO_4	25	48 hr	
1	10 ml CH_3CO_2H, 100% excess 30% H_2O_2	25	48 hr	
1	10 ml CH_3CO_2H, 100% excess 30% H_2O_2, 0.5 ml H_2SO_4	25	48 hr	
1	5 ml CH_3COCH_3, 5% excess $KMnO_4$	25	48 hr	Recovery of dinitroso comp'd
1	10 ml CH_3CO_2H, 5% excess $KMnO_4$	25	48 hr	
1	10 ml CH_3CO_2H, 5% excess $KMnO_4$, 0.5 ml H_2SO_4	25	48 hr	
1	10 ml CH_3CO_2H, 5% excess CrO_3 in 2-3 ml H_2O, 0.4 ml H_2SO_4	25	48 hr	
1	10 ml CH_3CO_2H, 5% excess CrO_3 in 2-3 ml H_2O, 0.4 ml H_2SO_4	85	30 min	
1	10 ml CH_3CO_2H, 5% excess CrO_3, 0.4 ml H_2SO_4	85	30 min	
5	50 ml 30% H_2O_2, 1 ml H_2SO_4	85	18 hr	Negligible water-insol. fraction, unidentified, mp 105 to 115°C

TABLE XXVIII

ATTEMPTED OXIDATION OF DI-(β-CYANOETHYL)-NITROSAMINE

Nitroso Comp'd g	Solvent	Reagent	Temp, °C	Time, hr	Product
1	10 ml CH_3CO_2H	1/3 excess 30% H_2O_2	25	48	Water-soluble products
1	10 ml CH_3CO_2H	1/3 excess 30% H_2O_2; 1 ml H_2SO_4	25	48	
1	10 ml CH_3CO_2H	1-2/3 excess 30% H_2O_2	25	48	
1	10 ml CH_3CO_2H	1-2/3 excess 30% H_2O_2; 1 ml H_2SO_4	25	48	
1	5 ml CH_3COCH_3	10% excess 10% $KMnO_4$	25	48	
1	10 ml CH_3CO_2H	10% excess 10% $KMnO_4$	25	48	
1	10 ml CH_3CO_2H	10% excess 10% $KMnO_4$, 0.5 ml H_2SO_4	25	48	
1	10 ml CH_3CO_2H	10% excess CrO_3, 0.4 ml H_2SO_4	25	48	

APPENDIX A

Report No. 686
SPIA/M3

Data Questionnaire on

COMPOUNDS FOR USE AS INGREDIENTS OF PROPELLANTS AND OTHER EXPLOSIVES

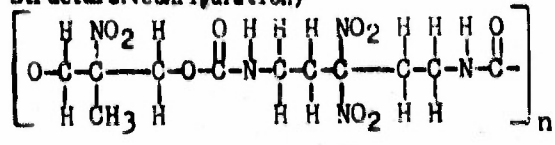
Listed below are the characteristics which are believed to be of importance in the study of a compound which may possibly be used as a constituent of solid propellants or other explosives. It is not expected that all this information will be available for every compound. For example, with a compound showing poor stability, it is probably not advisable to investigate that compound farther. After placing such information as is available for a compound which you have prepared or tested on one of these forms, send it to SOLID PROPELLANT INFORMATION AGENCY, APL/JHU, 8621 Georgia Avenue, Silver Spring, Maryland. As additional information on the same or new compounds accrues, forward it on a similar form at a later date. The information submitted on these forms will be rewritten and published by SPIA in loose-leaf manual form. These forms may also be used as work or data sheets for your experimental studies. Extra copies are available upon request from SPIA. Suggestions for improvement of these forms are invited. If insufficient space has been provided for any item, attach separate sheets.

COMPOUND: Polyurethane of 3,3-dinitro-1,5-pentanediisocyanate + 2-nitro-2-methyl-1,3-propanediol

Name _____

Empirical formula $(C_{11}H_{17}N_5O_{10})_n$

Structure: (configuration)



Information submitted by:
Activity Aerojet Engineering Corporation
Person J. R. Fischer, R. Parrette
Date _____

Preparation reaction(s): $n[OCN-CH_2CH_2-C(NO_2)_2-CH_2-CH_2-NCO] + n[HO-CH_2-C(CH_3)(NO_2)-CH_2OH] \rightarrow [C_{11}H_{17}N_5O_{10}]_n$

1. Quantitative analysis (% by weight)

	Carbon	Hydrogen	Oxygen	Nitrogen		
Calculated from formula	34.83	4.52		18.47		
By determination	35.28	4.52		18.23		

2. Burning properties: (compared to nitrocellulose, under nitrogen at atmospheric pressure:)

_____
(faster? slower? residue? etc.)

3. Stability and Sensitivity: Plot any graphs on separate sheet. Discuss methods used when they vary from references. Give temperature used. (Use separate sheet if necessary.)

Name of test	Recommended method	
a. Impact Sensitivity	OSRD 3185	
b. Thermal Stability	OSRD 3401 p.8	134.5°C, methyl violet paper
c. Vacuum Stability	OSRD 3401 p.10	
d. Temperature of Explosion	OSRD 3401 p.6	
e. Temperature of Ignition	OSRD 3401 p.6	
f. Thermal Stability, 65.5°C	Picatinny Arsenal No. 1101; 1.3-g sample, KI-starch paper.	
g. Impact Stability	Bureau of Mines, Bull. No. 346, 2-kg wt., 50% shots.	
h. Impact Stability	Same as g., but with 5/0 sandpaper on anvil.	

RESULTS OF ABOVE TESTS

	Reference compound (designation-TNT, Tetryl, N.C., etc.)	New Compound test results
a.		
b.	Nitrocellulose, 30 min, no color	No color or decomposition, 5 hr
c.		
d.		
e.		
f.	Nitrocellulose, 10 min, no color	No color, 5 hr
g.	RDX, 28 cm; composition A, >100 cm	>100 cm
h.	RDX, 33 cm; composition A, 55 cm	>100 cm

4. Heat of formation: (ΔH) $\pm$ -23 (Indicate sign) Kg. calories at 25°C., 1 atm. pressure

Report No. 686
SPIA/M3

	By Experiment	By Calculation	Method (Description or reference. Separate sheet if necessary.)
5. Energy of explosion (Q) (at 25°C, H_2O liquid)	_____ cal/gm	_____	_____
6. Heat of combustion (H_c) (at 25°C, H_2O liquid)	3625 cal/gm	3655	Aerojet Report 417A
7. Specific impulse (I_{sp}) calc:	_____ lb-sec/lb	_____	

8. Physical form of compound (viscous liquid, crystalline type, etc.) White, amorphous powder. Can be molded into light-yellow, clear, plastic specimen.

9. Simple microscope analysis data: _____ (crystal studies)

10. Density (Meare method) 1.467 gm/cm³. (Micro or other method) _____ gm/cm³. (Explain on separate sheet any unique methods you use.)

11. Index of refraction: ($n_D^{25°C}$) _____ 12. Color white 13. Odor None.

14. pH at 25°C. 5.8 (Method reference CSRD 3401 n.4, or CSRD 5968. Indicate method used, i.e. solvent and concentrations used. pH indicator paper or Beckman pH meter.) Water
Saturated solution, Beckman meter.

15. Hygroscopicity:

	New Compound	Reference Compound _____ (designation)
Visible change on exposure to ambient air.	_____	_____
% wt increase by* (a) or (b) (Strike out method (a) or (b) if not used.)	_____	(If other than below methods are used, explain on separate sheet.)

*Method:

(a) The sample (approx. 5-10 g. of whole grain small powder or 1 grain of large powder) is placed in a glass weighing bottle. The weighing bottle (cover removed) is placed in a vacuum drying oven for 5 hrs. @ 55°C. Remove weighing bottle from oven, cover with glass stopper, cool in a desiccator and weigh accurately. This is taken as original dry weight of sample. Then place weighing bottle (cover removed) in a humidor (a 10-in. desiccator is a satisfactory vessel) containing 1 liter of 18.6 ± .5% H_2SO_4. (This gives relative humidity 90 ± .25%). Place in an oven maintained at 30 ± 2°C. On the fourth day remove weighing bottle from the humidor, cover with glass stopper, cool in a desiccator and weigh. Then return to humidor for 24 hours, cool and reweigh. Continue daily weighings until constant weight indicates sample has reached equilibrium with 90% R.H. The % weight increase is then reported as hygroscopicity of the sample.

(b) An alternate method is in CSRD 3401 p.3.

16. Volatility: Report as rate of loss in wt % per unit area (for liquid samples measure the surface area; for solids, the sample should be screened between 100-120 mesh U.S. Standard certified sieve) per 4 hrs., after constant rate of loss is obtained during three consecutive 4-hr. periods at (a) 25°C in a vessel through which a stream of dry air is forced, (b) in an oven at 65.5°C or (c) under other test method or conditions. _____
(Description or reference to other test or conditions used. Use separate sheet if necessary.)

Volatility results on:	New Compound	Reference Compound _____ (designation)
a.	_____	_____
b.	_____	_____
c.	_____	_____

17. Boiling point, or decomposition temperature: _____ °C.
(underline which temperature is reported)

18. Heat of Vaporization: _____ g-cal./gm _____ BTU/lb.

19. Heat of Fusion: _____ g-cal./gm _____ BTU/lb.

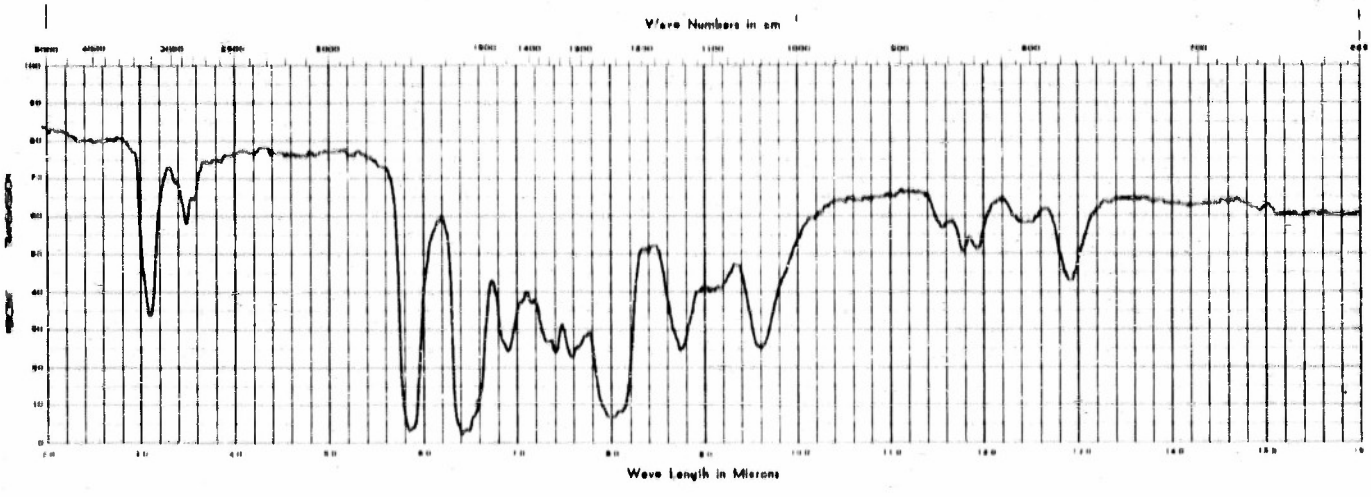
20. Melting point: _____ °C. Softening point range, 60 to 65°C.

21. Solubility of new compound:

< 0.01	g/100 ml	H_2O at 25°C.		at	°C.
0.016	g/100 ml	toluene (name material used as solvent)		at 25	°C.
< 0.01	g/100 ml	n-heptane (name material used as solvent)		at 25	°C.
0.050	g/100 ml	methanol (name material used as solvent)		at 25	°C.
0.031	g/100 ml	chloroform (name material used as solvent)		at 25	°C.

Very soluble in ethyl acetate and acetone.

22. Infrared Transmission Curve



Polyurethane I-J film, 0.0003 in. thick. 2-Nitro-2-methyl-1,3-propanediol with 3,3-dinitro-1,5-pentanediisocyanate. 12-min scan.

Under compatability we are considering the ability of two compounds to be in intimate contact (Note OSRD 5758 p. 21-22) over a long period of time without adverse effects on either the chemical or physical properties of either material. These tests will probably be of varied extent. They might be some of the following: (a) Standard stability tests. (b) Simple observations of exudation or separation at ambient or accelerated temperature. (c) Prepare thin sheets (.025" thick, 1" square) of the plasticized material. Separate the sheets with strips of cigarette paper or carbon paper and compress the stack in a "C" clamp. After several days note the oily collection on the paper. Please give reference to or describe procedure used. Item 26 is to indicate results when the compound is in contact with some material other than ethyl cellulose, nitrocellulose or rubber. Test performed by dissolving sample and standard in a common solvent, drying rapidly on a glass plate and examining the resulting film for clarity and homogeneity.

24. Compatability with ethyl cellulose:

25. Compatability with nitrocellulose: Ratio, wt sample / wt NC

20/80	Compatible
50/50	Compatible
80/20	Compatible

26. Compatability with rubber: Ratio, wt sample / wt rubber

20/80	Incompatible
50/50	Incompatible
80/20	Incompatible

27. Compatability with _____:

28. Polymerizing properties of the new compound:
   (a) By itself
   (b) In mixtures (with additives)
   (c) Inhibiting action on polymerization of:
      Thiokol
      Methacrylate
      Other compounds

29. Availability
   a. Amount now available? Research quantities.
   b. When was available material first prepared?
   c. Amount prepared at that time?
   d. Is large production feasible?
   e. Plant capacity in existance, lbs/day?
   f. Outline steps for a quantity production method

30. Additional information: (toxicity, hazards, deterioration, oxygen balance, detonation rate, explosive power, ease of hydrolysis by water, etc. List references, reports, data books, etc. that refer to the compound.)

APPENDIX B

MOREHOUSE SPEEDLINE MILL

A new Morehouse Speedline mill has been acquired for the precipitation of nitropolymers from solution. The precipitation of larger amounts of nitropolymers can be conducted in a short time.

Figure

Morehouse Speedline Mill

Report No. 686

N7onr-462, Task Order I

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